Recovery of wood extractives by flotation

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Abstract

Wood extractives from softwood species include resin acids, fatty acids and triglycerides. Their water repellency, adhesive properties and biological activity make them useful in manufacturing, agriculture and medicine with broader applications expected to be developed in the future with a shift toward renewable resources. These wood extractives can be problematic in paper manufacture as they cause deposits on machinery and in the paper products, which requires higher levels of maintenance, limits water recycling, increases wastewater toxicity and can reduce product quality. Current methods for addressing these problems in thermo-mechanical pulp (TMP) and paper mills include treatment of wood to reduce extractives content prior to pulping, tighter control of processes to prevent formation of deposits, and the use of additives to fix extractives into the paper product. None of these methods allow for recovery of the valuable wood extractives.

This thesis presents flotation as a viable method for recovery of wood extractives from TMP process water in pulp and paper mills. While flotation of wood extractives has been studied previously, it is not well understood in terms of the mechanism of flotation or its dependence on different variables. Furthermore, most published research relates to extractives from Norway spruce (*Picea abies*) which is a common plantation species in the northern hemisphere. By contrast, there are relatively few studies relating to Radiata pine (*Pinus radiata*) which is common in the southern hemisphere and contains a different composition of extractives.

The studies presented here investigate flotation of extractives from *Pinus radiata* TMP process water. Optimal flotation of wood extractives was achieved using 80 mg/L of added cationic surfactant dodecyltrimethylammonium bromide (DTAB) at pH 5 and 60 °C. This treatment reduced the extractives concentration by 95% and returned 90% of the water volume for recirculation.

The effects of different variables on flotation were studied and the results used to identify possible mechanisms of flotation. The most influential variables were the type of surfactant added, pH, and ionic strength. Flotation mechanisms proposed to explain the results included colloidal flotation, flotation of dissolved extractives as either surfactants or as complexes

with DTAB, and entrainment of fibres. Colloidal flotation appeared to depend on electrostatic attraction between air bubbles and wood extractive colloids which occurred either at low pH or with addition of a cationic surfactant. The efficiency of colloidal flotation was reduced by increased ionic strength, explained by compression of the electrical double layers around air bubbles and colloids by the electrolyte. Dissolved wood polymers also reduced colloidal flotation efficiency, presumably by inhibition of bubble-colloid attachment by steric hindrance. Flotation of dissolved extractives was proposed to occur at higher pH levels due to adsorption of resin and fatty acid anions on bubble surfaces by either surfactant adsorption or complex formation with DTAB. Fibre-bound extractives could be floated by physical entrainment of fibres in the froth.

Methods for recovery of extractives and DTAB from froth generated by the flotation treatment were also investigated. Maximum recovery of extractives was achieved by solvent extraction with a 60:40 mixture of ethyl acetate and heptane at pH 6 which recovered 88% of resin acids, 75% of fatty acids and 10% of triglycerides. Evidence of complex formation between wood extractives and DTAB was found which could explain the limited recovery of both extractives and DTAB from the froth.

Flotation is shown to be an effective laboratory method for removal and recovery of wood extractives from TMP process waters, that could be implemented in industry using existing machinery. The most effective surfactant additives have been identified as well as the most important process parameters and conditions that affect flotation efficiency. The influence of these variables on flotation has provided insight into the mechanisms of flotation to enable better control of flotation processes. Implementation of a flotation process for wood extractives recovery would reduce problems related to wood extractives and provide a valuable by-product. These benefits may offset the costs to make implementation feasible.

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Glossary

CMC	critical micelle concentration
CTAB	cetyltrimethylammonium bromide (hexadecyltrimethylammonium bromide)
DAF	dissolved air flotation
DLVO	Derjaguin, Landau, Verwey and Overbeek theory
DTAB	dodecyltrimethylammonium bromide
DTAC	dodecyltrimethylammonium chloride
GC	gas chromatography
IAF	Induced air flotation
TMP	thermo-mechanical pulp
SDS	sodium dodecyl sulphate
UPLC-MS	ultra performance liquid chromatography – mass spectrometry

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Chapter 1 General introduction and literature review

1.1 *Pinus radiata* wood extractives

The term wood extractives can include many different compounds that are extractable from wood by a variety of methods. In this dissertation however, the term is used to describe those lipophilic wood extractives that are released into process waters during thermo-mechanical pulping of softwoods. These extractives can also be extracted from wood using organic solvents. The wood extractives originate in parenchyma wood cells and resin canals and are produced by the plant for various purposes [1]. They make up only a few percent of the total dry wood weight, although different parts of the tree and different species contain different amounts and composition of extractives, with a clear contrast between the extractives from softwood and hardwood species [1]. Softwood is derived from conifer species which are commonly called pines or spruces. They share characteristics with their ancestors that were widespread during the Triassic period more than 200 million years ago, whereas hardwood is derived from flowering trees or angiosperms which evolved later during the early Cretaceous period [2].

Radiata pine or *Pinus radiata* is a softwood tree native to the central coast of California in the USA and two small islands off the Mexican coast [2]. It is a fast growing, medium density softwood that has been cultivated for over one hundred years. Though now under threat in its native location, it is a common plantation species in the southern hemisphere, used for paper production [2]. Norske Skog's paper mills in Australia and New Zealand process predominantly *P. radiata* wood [3].

The wood extractives released by thermo-mechanical pulping of softwood species can be categorised into three major classes of compounds: resin acids, fatty acids and triglycerides [4]. Example structures of these classes are given in Figure 1-1. In addition, there are also small amounts of various other compounds including sterols, sterol esters and waxes. A volatile component containing monoterpenes is largely lost to the atmosphere during wood pulping [4]. Hydrophilic or water-soluble compounds such as soluble carbohydrates and salts

are also released during pulping but they are not generally classed as wood extractives as they are not extracted by organic solvents.

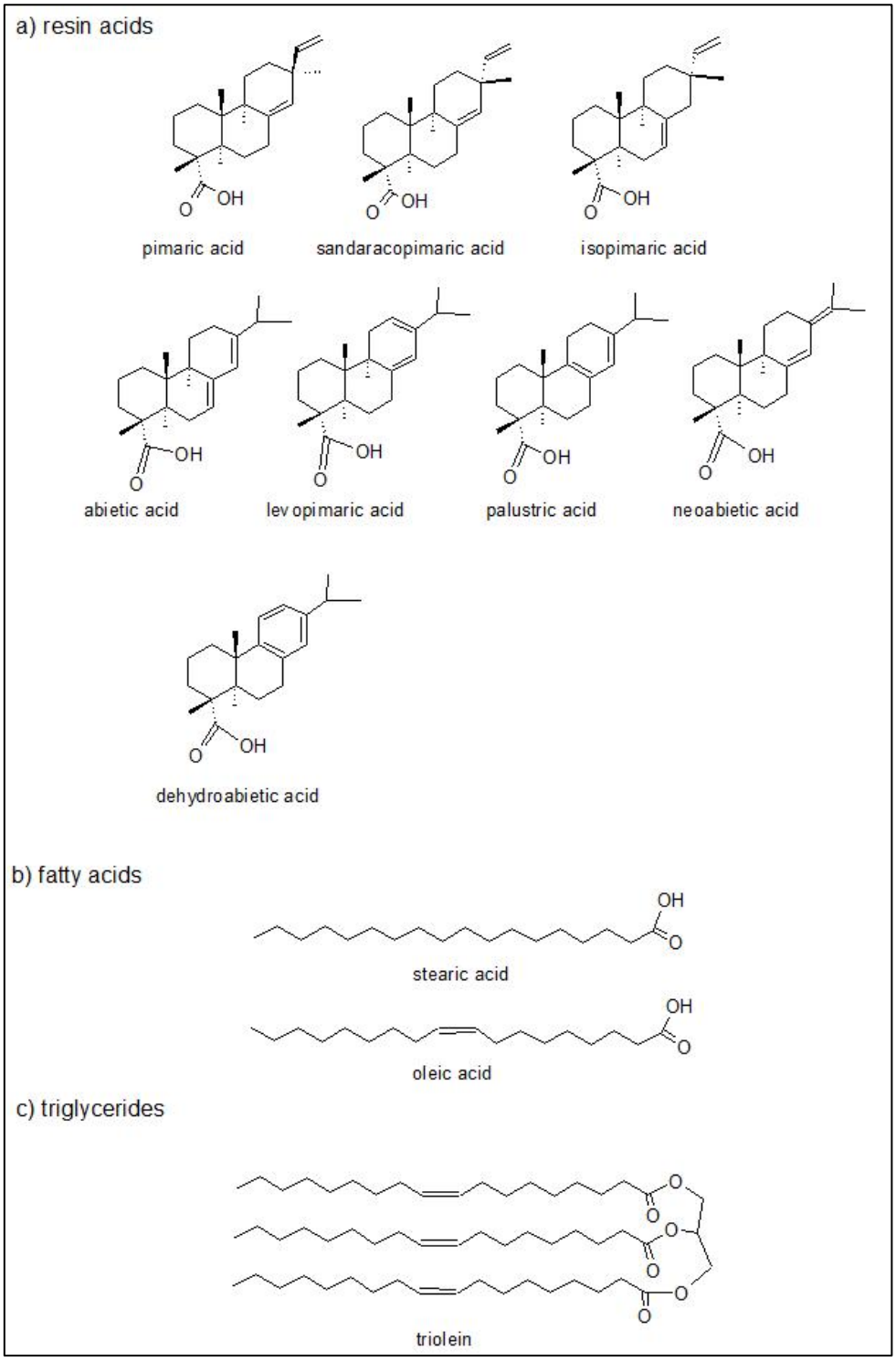


Figure 1-1 Structures of resin acids, fatty acids and triglycerides.

The resin acids are classed as diterpenes meaning that they are produced in the plant by linkage of 4 isoprene units [1]. They are found in the oleoresin which is produced by conifer species as a defence against bark boring beetles and the harmful fungi they carry [5, 6]. When the thick, sticky oleoresin mixture is secreted by the tree, it engulfs the attacking beetles and their fungal pathogens, killing them and impeding their attack. The volatile monoterpene component of the oleoresin evaporates, and the remaining resin acid component hardens to form a physical barrier that seals the wound in the tree and prevents further attack [7]. Structures of the eight most abundant resin acids in softwoods [4, 8] are shown in Figure 1-1 a). These can be divided into two groups based on their chemical structure. Firstly, the pimarane type resin acids in the first row which have a vinyl group attached at position C-13 and secondly, the abietane type resin acids, which have either an isopropyl or isoprenyl group in that position. The structure of different resin acids also results in differences in solubility. The pimarane type are less soluble than the abietate type resin acids and dehydroabietic acid is the most soluble due to the concentration of electrons around its aromatic ring which make the structure more polar [9]. A variety of fatty acids and triglycerides which originate in the parenchyma cells in wood also make up a portion of the wood extractives. Some example structures are shown in Figure 1-1 b) and c). Triglycerides are natural fats or oils and consist of three fatty acid molecules bonded to glycerol via ester bonds forming a single molecule. Oleic acid is the most abundant fatty acid in softwoods and triolein is the most abundant triglyceride [1, 8].

The resin acids and fatty acids are organic acids having the carboxylic acid group –COOH. This makes them weak acids as the hydrogen in the carboxylic acid group can dissociate in water to produce a positively charged hydrogen cation and a negatively charged anion [10]. The equation for this dissociation reaction is:

$$HA_{(aq)} \leftrightarrow A^-_{(aq)} + H^+_{(aq)} \qquad \text{[Equation 1]}$$

where ‘HA’ represents the un-dissociated acid molecule and A^- represents the conjugate base after dissociation of a proton. The two-way arrow indicates that the reaction is reversible. The extent of dissociation is given by the acid-dissociation constant (K_a) which is defined as:

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{[Equation 2]}$$

where $[H^+]$, $[A^-]$ and [HA] are the equilibrium concentrations of the hydrogen ion, conjugate base and acid respectively.

Rearrangement of this equation and incorporation of the definition of pH, gives the Henderson Hasselbach equation (Equation 5):

rearranged: $$[H^+] = K_a \frac{[HA]}{[A^-]} \qquad \text{[Equation 3]}$$

negative logarithm of both sides:

$$-\log[H^+] = -\log K_a - \log \frac{[HA]}{[A^-]} \qquad \text{[Equation 4]}$$

substituting in $pH = -\log[H^+]$: $$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad \text{[Equation 5]}$$

Thus, when $pK_a = pH$, then $\log \frac{[A^-]}{[HA]} = 0$, and $[A^-] = [HA]$. Therefore, the pK_a defines the pH value at which half the molecules are dissociated. The resin acids have pK_a values around 7 [11, 12] and the fatty acids have pK_a values ranging from 7 – 10 [12]. Therefore, above this pH most molecules will be dissociated and below it most molecules will be un-dissociated. Water solubility of these acids is also highly pH dependant because solubility increases dramatically upon dissociation due to the acquired charge. The solubility and pK_a values for some of the resin and fatty acids are listed in Table 1-1. The term “colloidal pK_a” is used to describe a pK_a value measured above the solubility limit [13].

Table 1-1 Solubility and pK_a values for some resin and fatty acids

	Solubility [mg/L] (20°C)	Colloidal pK_a (20°C)
Resin acids		
pimaric acid	2.17[a]	
sandaracopimaric acid	1.82 [a]	
isopimaric acid	1.70 [a]	7.08 [c]
abietic acid	2.75 [a]	7.26 [c]
levopimaric acid	2.54 [a]	
palustric acid	2.41 [a]	
neoabietic acid	2.31 [a]	7.07 [c]
dehydroabietic acid	5.11 [a]	6.77 [c]
Fatty acids		
Palmitic acid	0.69[b]	8.34 [c]
Stearic acid	0.56 [b]	9.89 [c]
Oleic acid	-	8.22 [c]
Linoleic acid		7.43 [c]
Linolenic acid		6.83 [c]

References: **a**- [9], **b**- [14], **c**- [12]

Resin and fatty acids and their anions are also surface active (also called surfactants) having in their structure a polar segment and a nonpolar segment [4] as depicted in Figure 1-2 a). The carboxylic acid group is polar, and upon dissociation is even more polar, whereas the molecule or anion body is nonpolar. Thus, the acids or anions adsorb at polar/non-polar interfaces including the air-water interface, colloid surface and on surfaces in contact with water. An important property of surfactants is their ability to form micelles in solution. Micelles are structures formed by groups of surfactant molecules arranged such that the hydrocarbon ends form a hydrophobic core and the solvated polar groups form an outer shell in aqueous solution, as depicted in Figure 1-2 c).

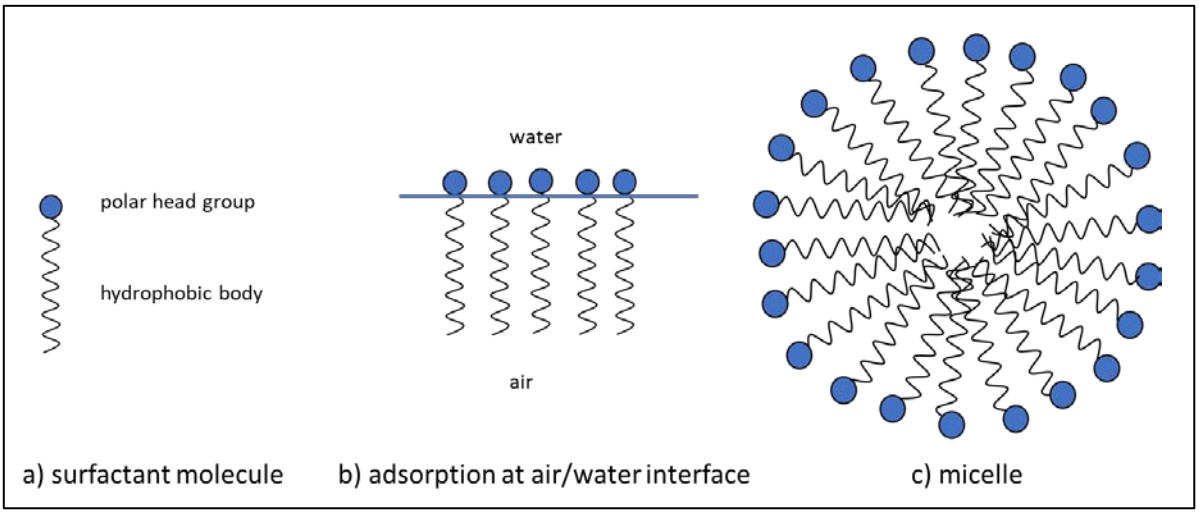


Figure 1-2 Surfactant structures

Micelles form above a certain surfactant concentration called the critical micelle concentration (CMC) which is dependent on conditions such as temperature and ionic strength [4]. Micelles can form from a single species or from a mixture of surfactants. They solubilise hydrophobic substances by absorbing them into their core [4].

Triglycerides are not acids, having no labile hydrogens [4]. As such, they remain as neutral molecules regardless of pH and have very limited solubility in water. They are also not surface active. Being nonpolar molecules, they are soluble in nonpolar solvents such as hydrocarbons and other fats or oils, and can also be absorbed into resin and fatty acid micelles. Triglycerides can hydrolyse under the action of lipase enzymes and during wood storage conditions to produce free fatty acids which can affect the composition of wood extractives [4].

The wood extractives found in different softwood species are similar, though *P. radiata* is known to have a higher proportion of resin acids in comparison with the more extensively researched *Picea abies* (Norway spruce), the major northern hemisphere species used for paper production [15]. The comparison of extractives components in wood pulp from these two species is presented in Table 1-2 which shows that *P. radiata* TMP contains roughly double the weight of resin acids and roughly half the weight of triglycerides.

Table 1-2 Extractives in *P. radiata* TMP compared *to P. abies* TMP

	***P. abies* TMP**	***P. radiata* TMP**
resin acids (g/kg)	2.00	4.55 ±1.02
fatty acids (g/kg)	0.40	0.50 ±0.18
triglycerides (g/kg)	4.55	1.49 ±0.33
reference	[16]	[15]

1.2 Value of wood extractives

The natural properties of wood extractives that protect the tree from insect and microbe threats also make them useful for a variety of human purposes. Their physical properties of water repellency and tackiness make them useful for waterproofing timber [17] and as additives in adhesives and rubber. Their chemical properties and biological activity against fungal and insect pathogens can be useful in medicine, agriculture and treatment of building materials [18-28]. Some of these properties can even be improved upon by using wood extractives as starting materials for synthesis of more active derivatives [27, 28]. Wood extractives can also be a source of organic molecules for more general chemical synthesis of a wider variety of compounds [29]. These useful properties of wood extractives have been exploited in different ways throughout human history [5]. Into the future, with new methods and knowledge, wood extractives may provide an important and sustainable source of materials for a variety of purposes [6].

Historically, oleoresin from conifer species was a major industry supplying pitch and tar for waterproofing of wooden sailing ships, as well as turpentine produced from the volatile component [1, 5]. As the era of wooden ships passed there was no longer such a need for waterproofing timber. The rise in petroleum production also provided a new resource for solvents, fuels and chemicals that could be obtained more cheaply. However, oleoresin is still produced commercially by extraction from wood and bark or by tapping live trees [6]. The crude oleoresin is refined by steam distillation into gum turpentine containing the volatile monoterpenes, and gum rosin containing the diterpenoids. Turpentine is used as a solvent and rosin goes into the manufacture of a wide range of products including adhesives, additives to rubber products, printing inks and paper sizing [5, 6, 30]. The global gum-rosin market is

expected to reach USD 2.49 billion by 2024 with increasing demand for higher grade product [31, 32]. There is however, a trend toward substitution of gum rosin with rosin derived from tall oil [31]. Tall oil is a by-product of the Kraft or sulphate process which is a widely used chemical pulping process that produces high quality cellulose pulp [33]. Crude tall oil is separated into fatty acids and resin acids (rosin). Recovery of the tall oil not only provides the industry with a valuable by-product but reduces problems caused by wood extractives if they remain in circulation in the pulp and papermaking process. These problems include reduction of process efficiency, scaling in evaporators, fouling of boilers, increased emissions and increased effluent toxicity [33]. The applications for tall oil rosin are limited, however, due to contamination with sulphur compounds which give the product an unpleasant odour and darker colour [34, 35]. Thus, purification is necessary to produce a higher grade product. Thermo-mechanical pulping does not involve the use of sulphur compounds and is therefore potentially a cleaner source of wood extractives with the potential to supply the existing market and developing new markets.

There has been renewed interest in wood extractives for wood treatments. Chemically benign treatments for timber are sought, particularly for use in decking, fencing and playground equipment where it is undesirable to use chemical treatments that might be harmful to people or the environment [17-19]. Mixtures containing wood extractives have been studied and found to be beneficial. Dahlen et al. [17] used resin acids from tall oil to treat decking boards and found that they provided water repellency for up to two years which reduced absorption of water by a third and splitting of the timber by a half. Temiz et al. [18] studied resin acid mixtures in combination with boric acid which is a wood preservative less toxic than arsenic or chromium but is prone to leaching due to its high solubility in water. Wood extractives, particularly resin acids in combination with boric acid provided protection against fungal rot and prevented leaching of the boric acid [18]. Likewise, Hien et al. [19] demonstrated the benefit of resin acids as a fixative for copper sulphate. The addition of the resin acids reduced leaching of the copper by half and reduced fungal decay [19]. As effective wood treatments utilising wood extractives are developed, and an awareness of the need for environmentally benign wood treatments grows, a larger market for wood extractives may also grow.

Wood extractives have value in medicine due to their bioactivity. Oleoresin has been used traditionally around the world as a medicine to treat wounds and infections. For example, in Lapland, Northern Finland, people have boiled oleoresin from *P. abies* with butter or animal fat to produce a salve used to treat wounds and skin infections for centuries [24]. In Turkey, oleoresin from the native *Pinus brutia* is used in traditional medicines to treat stomach complaints, skin wounds and infections, and to clean the mouth and teeth [23]. More recently, in the search for new bioactive compounds for pharmaceutical and agricultural industries, the activity of individual compounds has been studied. This has revealed many examples of effective activity that justifies those traditional remedies [7]. Soderberg et al. [21] studied the antibacterial activity of rosin from tall oil and individual resin acids and found activity against Gram-positive bacteria but not Gram-negative bacteria. Greater activity was found in the abietic type resin acids with most active being dehydroabietic acid [21]. With increasing drug resistance in human pathogens, there is growing interest in finding new antibiotic drugs. Antibiotic activity of resin acids against drug-resistant strains of human opportunistic pathogens have been reported. Isopimaric acid isolated from *Pinus nigra* cones was shown by Smith et al. to have activity against multi drug-resistant and methicillin-resistant strains of *Staphylococcus aureus* [22]. Dehydroabietic acid isolated from resin oil from *Pinus elliottii* was shown by Leandro et al. to be active against drug resistant *Staphylococcus epidermidis* [26]. Derivatives of resin acids can exhibit an even wider range of activities making them ideal starting materials for synthesis of a broader range of drugs. For example, Fonseca et al. reported antiviral activity of dehydroabietic acid derivatives [28] and Gigante et al. reported antiviral and anticancer activity of abietic acid derivatives [27]. Anti-inflammatory and anti protazoal activity have also been recently reported for derivatives of levopimaric and dehydroabietic acid respectively [20, 25].

There is a need for renewable sources of organic chemicals to replace the finite fossil sources of hydrocarbons, from which many modern chemicals are derived. Wood is a renewable resource when grown and managed sustainably. Thus, wood extractives may be a valuable alternative source of organic chemicals. James H. Clarke, a leading researcher in green chemistry, identifies waste materials from food and manufacturing as valuable future sources of chemicals [36]. He argues that to achieve a stable and sustainable economy, society must recognise and look toward these opportunities. Currently, wood extractives are a waste

material from thermo-mechanical pulping that cause problems in the processing of wood fibre and must be treated by biodegradation before they can be discarded. Alternatively, recovery of these extractives may provide high grade products for current and new industries that develop in a shift to a circular economy.

1.3 Problems caused by wood extractives in pulp and paper industries

In paper manufacture world-wide, water-immiscible wood extractives cause significant problems[4, 37-40]. Paper and cardboard products are made from the cellulose and lignin fibres in wood, with the first step in production being pulping, to chemically or mechanically break apart the wood cells into smaller fragments. Wood extractives enter the process at this stage as they are released from the wood cells and resin canals. Their presence has detrimental effects throughout paper production and printing processes. These include pitch deposits, reduced paper quality, runnability problems for printing machines, limitation of water saving measures and increased toxicity of waste waters. These problems are more pronounced for thermo-mechanical pulp mills that process wood species high in extractives such as Norske Skog's mills in Australia and New Zealand [15]. A variety of methods are implemented in pulp and paper mills to reduce and manage the problems caused by wood extractives [4, 38, 39]. They include pre-treatment of wood, process control to prevent deposits, the use of additives that fix extractives into the product, and biological treatment of effluent waters.

Pitch deposits on machinery occur when the colloidal suspension of wood extractives formed during pulping is destabilised, causing the colloids to aggregate and deposit [39]. Much research has been done to identify and understand causes of destabilisation and deposition which is a complex interaction of factors including extractives composition, pH, salt concentrations, dissolved wood polymers, sheer forces and fibre [15, 40-60].

At Norske Skog's Australian paper mills, which process *P. radiata*, the composition of pitch deposits has been analysed, as have the factors that contribute to colloidal instability. A study of deposits on machinery in 2008 revealed high levels of wood extractives including fatty acids, glycerides and particularly resin acids and resin acid salts in the deposits [61].

Deposition was correlated to extractive levels measured in process water [61]. At one location, high fibre-bound extractives were identified as the major cause of deposits and at another, inefficient mixing of soda ash for pH control caused dissolution of resin acids and subsequent formation of insoluble aluminium resinates [61]. In both cases the problems were then able to be managed to prevent severe deposition. Further research into causes of pitch deposition at Norske Skog's Albury mill identified important factors in colloidal stability [59]. Soluble calcium, shear forces and downward temperature shock all destabilised colloids. Dissolved organic wood polymers and pH were also important. The ester to acid ratio (EAR) was identified as a useful indicator to explain the observed seasonal pattern of pitch depositions [59]. The EAR was defined as the ratio of glycerides (of fatty acids) to free fatty and resin acids. In summer months when the EAR was lower, pitch deposition worsened. A lower EAR was proposed to affect colloid stability by changing the extent to which fatty acids share the surface of the colloid [59].

Paper product quality is affected by increased wood extractives in the pulp, and by deposits occurring in the paper machines and on the paper [4]. Wood extractives incorporated in paper reduces its strength by limiting hydrogen bonding between cellulose fibres. Deposits in paper can cause visible specks or variations in thickness and deposits on machinery can produce holes or imprints in the paper. Resin acids in paper used for food packaging is of concern as they have been shown to be toxic to human cells [62], although, the levels that migrate into food products has been shown to be well below the recommended exposure limit [63]. Resin acids are also responsible for contact allergies to wood products including paper from thermo-mechanical pulp (TMP) [63].

Excess levels of wood extractives in paper can also cause problems for printing machines. The presence of extractives changes the chemistry of the paper surface inhibiting bonding of glues and printing inks [4]. Deposits of extractives can occur on printing rolls too, causing holes and printing defects [4].

Water saving measures in pulp and paper mills are limited by the presence of wood extractives because closure of process water circuits allows the extractives to accumulate [38, 39]. At Norske Skog's mills in Australia and New Zealand, problems related to deposits have

been exacerbated in recent years by increased closure of process water circuits to reduce consumption of fresh water resources in-line with best practice manufacturing principles [59, 64]. In Australia there is increasing pressure to reduce freshwater consumption especially in drier locations such as Albury where one of Norske Skog's mills is located [65].

Wood extractives, particularly the resin acids are a major contributor to the toxicity of TMP effluent [4]. Resin acids are toxic to aquatic life including fish and plankton [9]. The extractives must therefore be removed from wastewaters. Common treatment is by biological degradation before release into the environment [4, 66].

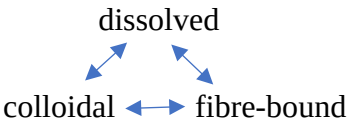
Various strategies are employed in pulp and paper mills to reduce these problems. Improved understanding of colloidal stability and increased process automation has enabled tighter control over processes to prevent conditions that destabilise colloids which can reduce pitch deposits [4]. The use of additives is also common. Mineral adsorbents such as talc, bentonite, and kaolin can fix extractives into the paper product thus removing them from the system. Additives that cause agglomeration such as aluminium compounds can also be used to increase the effectiveness of adsorbents [39]. Cationic polymers, known as retention aids are also used. These flocculate extractives particles or colloids, so they are fixed into the paper product [4, 38, 39]. However, disadvantages of these treatments are the cost of additives and changes to paper properties with incorporation of extractives and additives. Alternatively, the wood extractives content of wood chips can be reduced before pulping by mechanical compressive pre-treatment [67] or enzyme treatment [68] thus reducing problems in down-stream processes. Most of these current approaches to managing wood extractives in TMP mills do not allow for recovery of the extractives as they are either subject to biological decomposition, fixed in the paper product or collected in waste water.

1.4 Wood extractive colloid structure and stability

1.4.1 Wood extractives phases in TMP process water

The high temperatures and grinding action of thermo-mechanical pulping releases wood extractives into the process water. Being lipophilic, wood extractives have limited solubility and exist in three phases; dissolved, colloidal and fibre bound. The proportion of extractives

in each phase is highly dependent on conditions such as pH, temperature and extractives composition [69, 70]. Even under constant conditions, there is a dynamic equilibrium between the three phases in which individual molecules move between phases even as overall proportions are maintained.



The pH dependence of phase distribution was the topic of a doctoral thesis by Strand [70]. By studying lab-prepared dispersions of extracted wood pitch, it was found that the phase distribution was strongly dependent on pH with almost all acids in the colloidal phase at pH 3 and increasingly present in the dissolved phase at higher pH. The presence of salt resulted in dissolution at higher pH, while a lower ratio of neutral pitch resulted in dissolution at lower pH. The movement of resin and fatty acids between phases with sudden pH change was found to be very fast.

1.4.2 Structure

Wood extractive colloids are spherical particles around 0.1 -3 µm in diameter [4, 60, 71]. Research has shown that their structure consists of a hydrophobic core containing triglycerides and other neutral compounds surrounded by an outer shell containing the more polar compounds such as resin and fatty acids [52, 72]. This structure is depicted in Figure 1-3. The nonpolar sections of the resin and fatty acid molecules embed beneath the colloid surface with the polar carboxylic acid group at the surface, oriented toward the water phase. Research by Lee et al. suggests that in *P. radiata* wood extractive colloids, the fatty acids form a mobile intermediary shell between the surface shell and the core [73]. The location of the fatty acid shell was found to change with the proportion of triglycerides. At low triglyceride levels the fatty acids were drawn into the core, while at high triglyceride levels they were pushed towards the surface [73]. This is particularly important for *P. radiata* which has a much higher resin acid component than does *P. abies* on which previous studies were based.

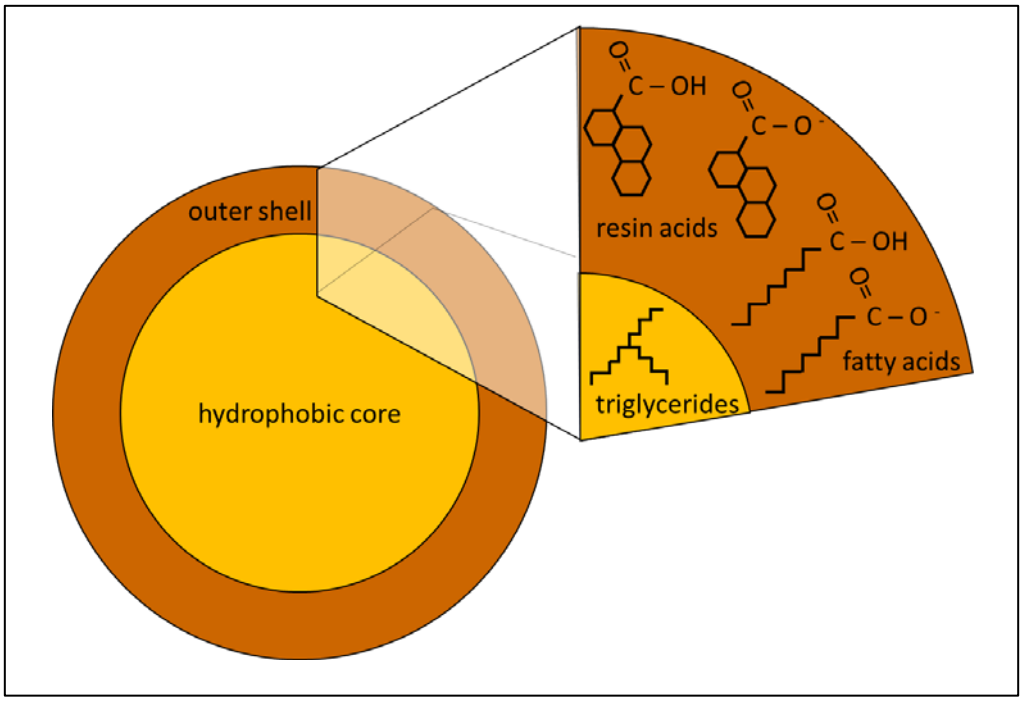


Figure 1-3 Wood extractive colloid structure

1.4.3 Electrical double layer

Wood extractive colloids are negatively charged at the surface due to the ionisation of carboxylic acid groups. This creates an electrostatic field around the colloid that affects the composition and structure of the surrounding solution forming what is called an electrical double layer. This is depicted in Figure 1-4.

The electrical double layer consists of two regions. The inner Stern layer comprises counter ions that are adsorbed strongly enough to overcome thermal agitation, while the outer diffuse layer beyond this, is influenced by electrical forces and thermal motion [74]. The distance at which the surrounding fluid becomes mobile under kinetic conditions is called the shear plane or slipping plane. The electrostatic potential at this point can be determined from electrophoretic mobility measurements and is called the zeta potential [74].

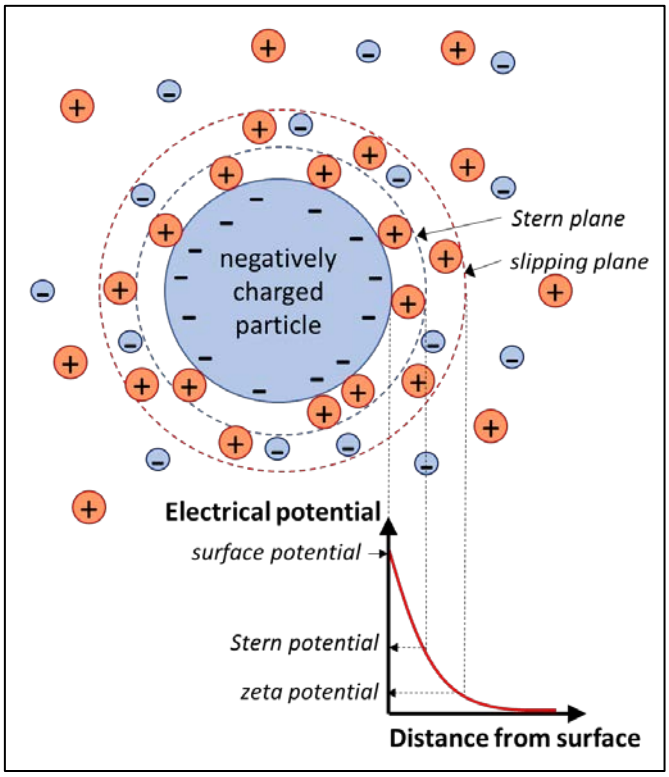


Figure 1-4 The electrical double layer around a negatively charged particle in aqueous solution.

The electrical potential decreases exponentially with distance from the particle surface. The Debye-Hückel approximation of the Poisson-Boltzmann equation gives the electrical potential, Ψ (mV) as a function of distance (x) from a spherical particle:

$$\Psi = \Psi_0\left(\frac{r}{x}\right) . e^{-\kappa(x-r)} \qquad \text{[Equation 6]}$$

where:

Ψ_0 = electrical potential at the surface,
x = distance from the centre of the particle,
r = radius of the particle,
and κ is given by the following equation:

$$\boldsymbol{\kappa} = \sqrt{\frac{2000F^2I}{\varepsilon_0\varepsilon_r RT}} \qquad \text{[Equation 7]}$$

where:

F = Faraday constant (= 9.6485 x 10^4 C.mol^{-1})

ε_0 = the permittivity of free space (= 8.8542 x 10^{-12} $C^2.N^{-1}.m^{-2}$)
ε_r = the dielectric constant of the solution (a dimensionless ratio)
R = the gas constant (= 8.314 $J.mol^{-1}.K^{-1}$)
T = temperature (in K)
I = ionic strength given by $\frac{1}{2}\sum c_i z_i^2$ in which:
c_i = concentration of ion species (in $mol.L^{-1}$)
z_i = valency of ion species
[74, 75]

The quantity κ with dimensions of m^{-1} is often inverted to give 1/κ, called the Debye length which gives a measure of the range or size of the electrical double layer [75]. As can be seen in the equation, apart from some fundamental constants, κ is dependant only on temperature and ionic strength which is a function of electrolyte concentration and valency. According to the equation, a higher electrolyte concentration or valency will increase κ and decrease the Debye length which is often described as compressing the electrical double layer.

1.4.4 DLVO theory

The quantitative theory explaining the stability of colloidal dispersions in water is called DLVO after Derjaguin, Landau, Verwey and Overbeek, who developed it in the 1940s [74, 76, 77]. The theory describes the potential energy changes as colloidal particles approach one another. These energy changes are a result of forces between the particles. The forces considered in DLVO theory are van der Waals forces which are short range attractive forces between molecules, and electrostatic forces due to the overlap of electrical double layers, which for like-charged particles, are repulsive. Both the van der Waals and electrostatic forces increase as the particles approach one another but at different rates. The sum effect of these forces gives the potential energy of interaction which is represented in Figure 1-5.

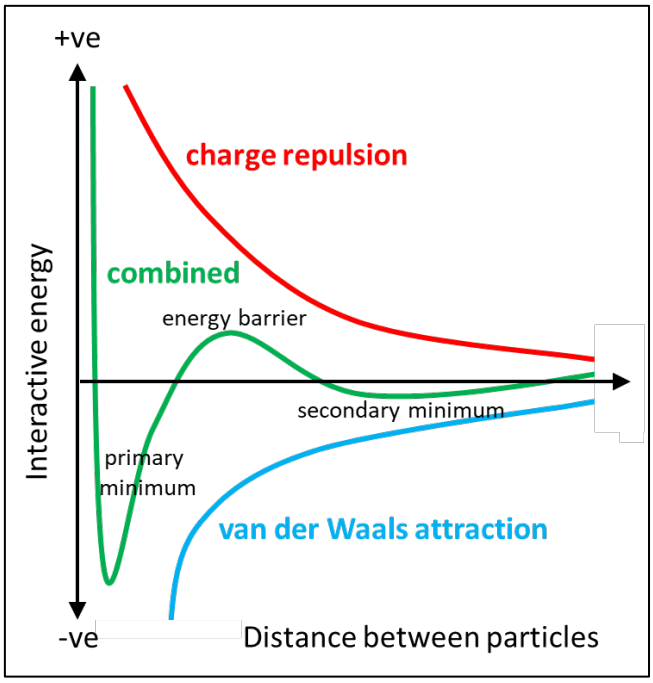


Figure 1-5 Potential energy between equal charged particles in solution

The red trace shows the potential energy due to electrostatic repulsion (positive) which decreases in magnitude with greater distance between particles. The blue trace shows the potential energy due to van der Waals attraction (negative) which also decreases in magnitude with distance but at a steeper rate at close range. The green trace shows the sum of both energies which is characterised by a maximum and two minima. The maximum forms an energy barrier which prevents particles from coming together, thus stabilising the colloidal dispersion. However, the relative size of the maximum and minima vary with changes to the electrical double layer which is affected by the particle charge and by electrolyte concentration in the surrounding medium. Increased particle charge increases electrostatic repulsion and raises the energy barrier stabilising the colloids. Increased electrolyte concentration has the opposite effect, reducing the Debye length and compressing the electrical double layer to a smaller radius around the particle which results in a reduced energy barrier. A low energy barrier can be overcome by the momentum of particle collisions resulting in attraction between the particles at the primary minimum which causes destabilisation of the colloidal dispersion and coagulation. This can be termed ‘coagulation at the primary minimum’[78]. Under some conditions, coagulation can occur at the secondary

minimum although the attachment is generally weaker and often reversible because the secondary minimum is relatively shallow [78].

The interaction energy due to attractive van der Waals forces (V_A) between two like particles is given by:

$$V_A = \frac{A \times r}{12 \times H} \qquad \text{[Equation 8]}$$

where:

H = the distance between two particles in a vacuum
r = the radius of both particles
A = the Hamaker constant
[4, 74]

The Hamaker constant is proportional to the square of the particle density, so is higher for more dense substances [4]. The van der Waals interaction energy is lowered by a liquid medium between particles, in which case an effective Hamaker constant applies. An approximation of the effective Hamaker constant for interaction of particle 1 across a medium 2 with particle 3 becomes:

$$A_{123} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{22}}\right) \qquad \text{[Equation 9]}$$

[74]

1.4.5 Factors affecting colloidal stability

Much work has been done towards identifying and understanding the factors that affect wood extractive colloid stability, particularly by researchers from Åbo Akademi University in Finland as well as the Australian group based at University of Tasmania [15, 40-60]. The Finland studies utilise wood extractives from *P. abies* or *P. sylvestris* species whereas the Australian studies have focused on *P. radiata*.

Added electrolytes have been shown to induce aggregation by destabilising wood extractive colloids as predicted by DLVO theory [41, 46, 47, 53-57]. Also, as predicted by DLVO theory, calcium and magnesium ions being divalent have a stronger influence on destabilisation than single valence sodium or potassium ions [53, 54, 57]. Calcium chloride

and sodium chloride are used to induce aggregation in the studies of other influencing factors [42, 44, 58, 60].

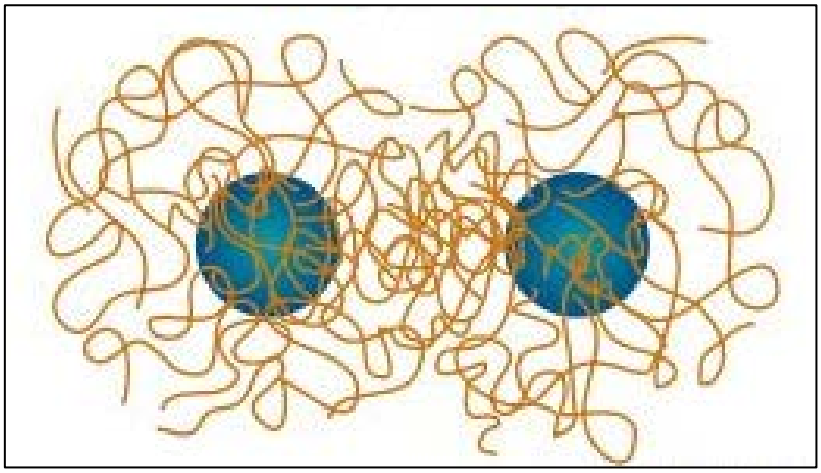


Figure 1-6 Steric stabilisation of colloids

One important factor in the stabilisation of wood extractive colloids that is not covered by classical DLVO theory is steric stabilisation [42, 46, 47, 51, 74]. Steric stabilisation is the prevention of colloidal coagulation by the steric hindrance of bulky molecules that physically prevent colloids from approaching each other. This is depicted in Figure 1-6. In TMP process water there are a variety of substances that provide this effect. These include wood polymers such as hemicelluloses, lignin and lignans [42, 46, 47, 51, 60]. The presence of these substances can effectively stabilise the colloidal suspension in otherwise destabilising conditions such as high electrolyte concentration or low particle charge due to low pH [42, 46, 47, 51, 60]. However, interaction between calcium and wood polymers under certain conditions has also been observed to lead to aggregation [41, 60].

Other factors investigated have included fibre, the composition of extractives, pH, shear and temperature. In one study, cellulosic fibres were shown to destabilise wood extractive colloids by adsorbing glucomannans thus removing the steric stabilisation otherwise provided by the glucomannans [43]. In Australian *P. radiata* mills, pitch deposits have been associated with high resin acid content [40] and seasonal variation in wood extractive composition, with high fatty acid and low glyceride ratio in summer leading to increased pitch deposits [45, 59]. Stability against salt-induced aggregation has been observed to increase with pH, explained by the higher charge on colloids with pH [58]. Higher shear has been shown to reduce colloid

stability [48, 58] and higher temperatures to increase it [45, 58], although, another study reported the opposite effect with increased temperature [48]. The interactions that lead to deposition are complex and change with the pH and temperature which not only affect colloid stability but colloid composition due pH dependent solubility and deprotonation of extractive components [50, 52].

1.5 Flotation theory

The first industrial flotation methods were developed in the late 19th century for separating minerals. Further development during the 20th century revolutionised the mining industry by making the processing of complex minerals economically feasible. The principle behind flotation is the adsorption of hydrophobic particles at the air-water interface, allowing them to be transported to the surface of water by bubbles [79]. This principle is also applicable outside the mining industry and consequently various flotation methods are now used in a wide range of other applications including potable water treatment, wastewater treatment, oil and coal recovery, and in the pulp and paper industry for deinking of recycled paper pulp and fibre recovery. The methods vary greatly as they have been adapted to optimise flotation of different materials.

Mineral flotation generally proceeds by the following steps:

1. Complex minerals are first crushed or ground into fine particles, a process which is called liberation. The particle size must be smaller than the mineral grains so that impurities and the desired mineral can be separated.
2. The particles are then mixed with water to form a slurry and an additive called the collector is added to render the desired mineral hydrophobic. The collector is commonly a surfactant that selectively binds to the mineral of interest changing its surface from hydrophilic to hydrophobic.
3. A second additive called the frother is added which alters the air-water interface to increase attachment of particles and allow formation of a stable froth.
4. The slurry is introduced to a flotation cell in which air bubbles are generated. The hydrophobic particles are transported to the surface by the bubbles forming a froth layer.

5. The froth containing the desired mineral particles is removed from the surface.

The process is illustrated in Figure 1-7 which shows separation of hydrophobic particles from a slurry in a flotation cell.

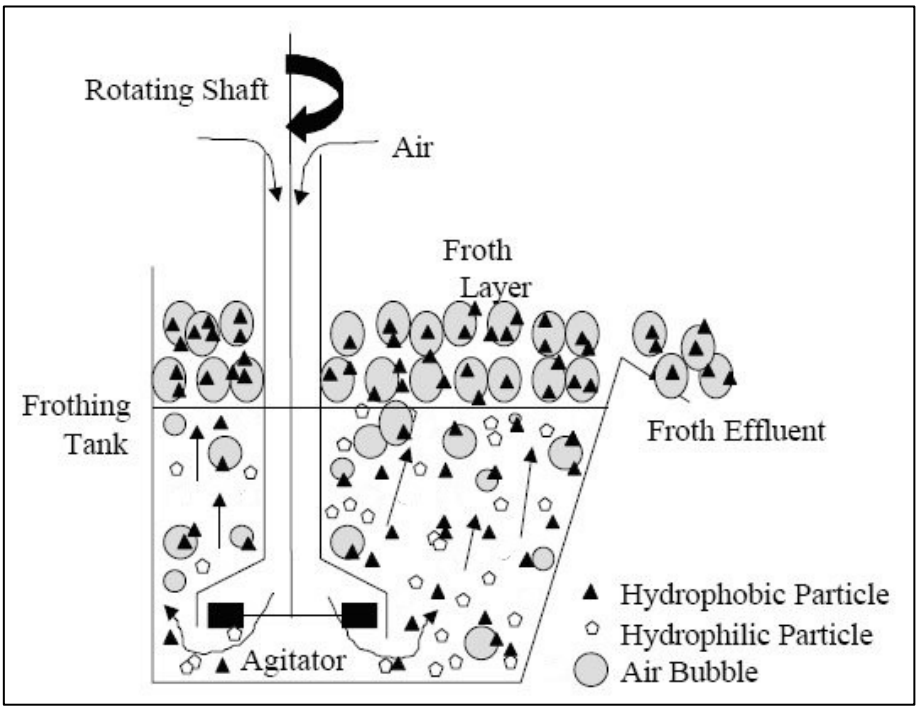


Figure 1-7 Mineral flotation

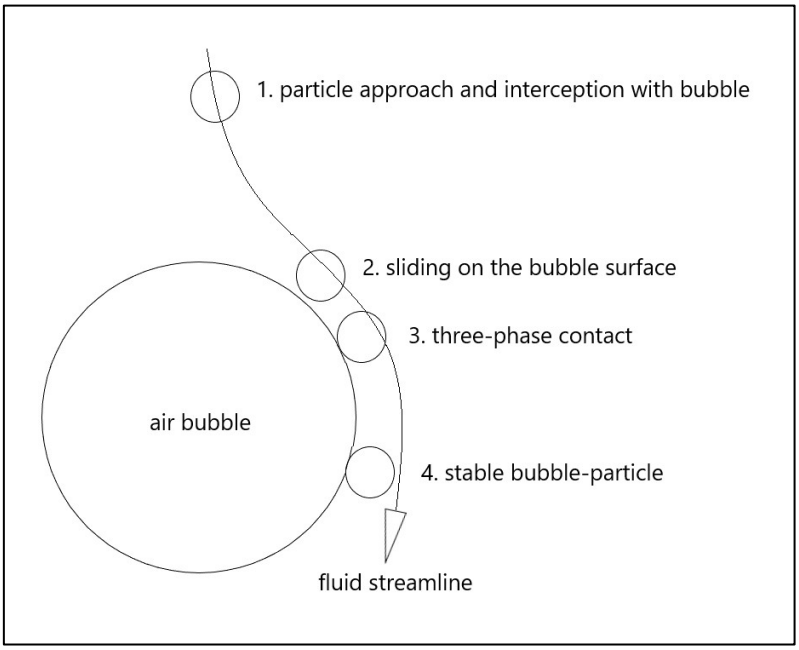


Figure 1-8 Attachment of particle to bubble

Much work has been done over the years to understand the fundamental processes behind effective mineral flotation which also applies in general terms to other flotation applications. The overall efficiency of a flotation process can be divided into sequential steps with associated probabilities of success [80, 81]. The steps can be modelled mathematically for specific conditions but are described here only qualitatively and depicted in Figure 1-8.

The interception of a particle with a bubble occurs when the two become close enough that surface forces and thin film dynamics become significant. This happens as bubbles and particles move through the fluid in the turbulent motion produced in the flotation cell or as bubbles rise to the surface. Large or dense particles with sufficient inertia can intercept the particle though collisions, whereas smaller or lighter particles tend to follow flow lines around a bubble and can intercept it only from the direction of flow or by diffusion. The probability of this step occurring is governed by many factors including particle size and inertia, bubble size, hydrodynamic forces, and fluid dynamics. The particle then slides over the surface of the bubble, separated by a thin film of liquid. If the sliding time is long enough for the liquid film to thin sufficiently, the film will rupture forming three-phase contact between the particle, fluid and bubble. The probability of this occurring is dependent on the disjoining pressure which is a measure of the film strength and is determined predominantly by short range van der Waals and electrostatic forces [82]. Inertia of the particle and hydrodynamic forces also play a role by influencing the sliding time. The hydrophobicity of the particle determines its contact angle with the liquid to favour three-phase contact. Upon formation of three-phase contact a bubble-particle aggregate is formed which must have sufficient stability to rise to the surface and form a froth layer. The stability is a balance between the strength of attachment and the forces that that may lead to detachment such as weight of the particle and hydrodynamic turbulence.

While this theory has been developed for mineral flotation, it has been applied to other applications including ink flotation from recycled paper pulp which was found to follow the same fundamental steps [80]. Alternative mechanisms for related flotation processes have been described in the literature as summarised in the following paragraphs [83-88].

Flotation of surface active molecules or surfactants can occur by adsorption on bubble surfaces. This mechanism is utilised for the removal of surfactants from wastewater and may be called foam fractionation [84]. In flotation of surface active molecules, individual molecules intercept bubbles by diffusion and adsorb at the air-water interface in a monolayer. Addition of a foaming agent may not be necessary since the molecules themselves, are foaming agents.

A mechanism relying only on surface forces for attachment (rather than three-phase-contact) was first proposed by Derjaguin for very small colloidal particles [87]. For particles of the order of 1-10 μm the gravitational and hydrodynamic forces that might detach the particle from a bubble are very small and can be balanced by surface forces alone without the need for three-phase contact. For this reason, Derjaguin called this ‘contactless flotation’. As in DLVO theory, the surface forces include van der Waals forces and electrostatic forces due to electrical double layer interactions, in this case between the air bubble and particle rather than between two particles. In theory, this mechanism of attachment is possible where the electrostatic repulsion is low enough to produce a net surface interaction energy of attraction which may occur at either the first or second minimum. Thus, attachment is due to primary or secondary minimum coagulation. Derjaguin suggested two methods for producing this result. One, by increasing the electrolyte concentration, the electrical double layers are compressed allowing van der Waals forces to dominate, and two, by introducing a cationic surfactant that will adsorb on the bubble surface reversing its charge. For wood extractive colloids, another option for reducing particle charge is lowering the pH since this will reduce the proportion of ionised resin acids at the surface. Several experimental studies have reported evidence for this mechanism including flotation of aluminium oxide [86] and wood extractive colloids [85].

Physical entrainment is a mechanism by which particles are physically trapped or entrained in the liquid surrounding bubbles. This mechanism is responsible for undesired impurities in mineral flotation and the undesirable loss of fibre in de-inking flotation [89]. Flotation by entrainment tends to be proportional to the liquid component in the froth and therefore drainage of excess liquid from the froth can reduce its effect. In other applications however, entrainment can improve the flotation outcome. For example, in less selective processes such as flotation of suspended solids from wastewater or fibre recovery in pulp mills, physical

entrainment mechanisms contribute to flotation efficiency [83]. The addition of flocculants and use of dissolved air flotation (DAF) in these processes also improve flotation by entrainment. Flocculants bind multiple particles together forming larger particles or flocs that are more easily floated. DAF systems create bubbles by the release of air-saturated pressurised water in the bottom of a tank. Very small micro-bubbles are formed under these conditions which can become physically trapped in the flocs. Bubbles can even nucleate on the flocs or particle surfaces which bypasses the need for bubble-particle interception.

A summary of the flotation mechanisms described, is given in Table 1-3. They have been ordered according to the size of the floated particles as this seems to be an important indicator of the mechanism.

Table 1-3 Flotation mechanisms

mechanism of attachment	**surfactant adsorption**	**surface forces**	**three-phase contact**	**physical entrainment**
particle size	molecular	small < 10 µm	medium 10 < 150 µm	Macro >150 µm
terms	-foam fractionation	-contactless flotation -micro-flotation	-froth flotation -mineral flotation -ore flotation -deinking	-macro flotation
applications	-separation of surfactants from wastewater -protein removal	-wood extractive colloid flotation	-mineral flotation -deinking of recycled paper	-suspended solids removal from wastewater -fibre recovery
bubble-particle interception	diffusion/Brownian motion	diffusion/Brownian motion	collision/inertial forces	collision/inertial forces
additives	none	opposite charged surfactant	collector and frother	flocculants

Because flotation methods have been applied across a broad range of fields which borrow or introduce terminology, there is no consistent classification of methods despite a system proposed in 1967 [84]. The mechanisms of flotation were also often elucidated after development of the techniques, so many of the terms used do not infer a particular mechanism, and in many cases more than one mechanism may operate. It is evident from the literature however, that the particle size is a large factor in determining which flotation

mechanism dominates. Wood extractive colloids are reported to have particle sizes less than 10 μm [71], and therefore may be floated by the surface forces mechanism, attached to bubbles by surface forces.

1.6 Flotation of wood extractives

Although flotation has been recognised as a potential method for removing wood extractives from process waters in pulp and paper mills, it has not to date been adopted by industry. Although published literature on the topic is limited, some promising results have been reported [40, 64, 85, 90-102]. Methods have varied and include foam fractionation, column flotation, DAF and induced air flotation (IAF) which produces bubbles by the mechanical action of an impeller. It may be, that pressure on industry to implement such processes has not been sufficient to justify the investment required. However, as requirements for environmental control and waste recovery increase and the potential for renewable sources of chemicals is recognised this may change. The available research published on flotation of wood extractives is listed in Table 1-4 and will be summarised in the following paragraphs.

Table 1-4 Research published on flotation of wood extractives

Authors	Year	Country	Water source	Flotation apparatus	Reference
Ng	1977	Canada	Kraft mill	foam separation	[90]
Richardson et al.	1996	Australia	TMP	DAF	[40]
Tay	2001	Canada	newsprint paper machine	column	[91]
Korpela	2002	Finland	TMP	not specified	[92]
Makris	2003	USA	Kraft mill	foam separation	[93]
Richardson and Grubb	2004	Australia	TMP	DAF	[64]
Negro et al.	2005	Spain	Kraft mill	DAF	[94]
Saarimaa et al.	2006	Finland	TMP	DAF	[95]
Korpela	2006	Finland	TMP	IAF	[85]
Haapala et al.	2010	Finland	TMP	IAF	[96]
Opedal et al.	2011	Norway	TMP	DAF	[97, 98]
Zasadowski et al.	2012-2016	Sweden	TMP	IAF	[99-102]

Flotation of wood extractives has been studied since at least the 1970s when Ng investigated foam separation as an alternative method for detoxification of Kraft mill effluent to meet the

environmental requirements of the day [90]. Ng recognised that the resin and fatty acids which were most problematic, were also surface active, enabling removal by flotation. He found foam separation to be successful at high pH where the acids were deprotonated and able to adsorb at the air-water interface forming a foam. At acid pH where there were no inherent surfactants, he found that addition of cationic surfactants enabled detoxification. He noted that this process was not viable on a large scale due to the expense of the surfactant unless it could be recovered in some way and did not further develop this method. He developed a foam separation method for caustic effluent using a 1.5 m flotation column and reported 66% removal of resin acids. His method was trialled in the field as well as the laboratory.

Makris also investigated the potential for resin and fatty acid removal from Kraft mill effluent by foam separation, focussing on their partitioning to suspended solids to aid removal at acid pH [93]. He developed a method using a 1.2 m flotation column which reduced the concentration of resin and fatty acids by an average of 25% with the volume loss less than 1%. Resin and fatty acid removal correlated with total suspended solids removal.

In Australia, Richardson et al. investigated the use of DAF with flocculants for removal of dissolved and colloidal wood extractives from whitewater in a mill processing TMP from *P. radiata* and recycled fibre [40]. Removal of colloidal material was successful, particularly from the most concentrated waters. However, this represented only 10% of the total wood extractives entering the process, so it was not considered to be an effective way to reduce the overall extractives in circulation. Removal of dissolved extractives was less successful and was explained by the inability for dissolved substances to flocculate. Later, in 2004, Richardson and Grubb again investigated DAF for removal of wood extractives from *P. radiata* TMP process water [64]. Using a lab scale flotation cell, they reported 80-90% removal efficiency for fibre bound and colloidal extractives but only 30% for dissolved extractives. They tested various additives to improve the removal of dissolved extractives but concluded that the most effective approach was to maintain a high colloidal and fibre bound fraction by pH control.

Tay investigated flotation as one of several possible methods for removal of wood extractives from newsprint machine whitewater and achieved good removal of resin and fatty acids [91]. A 98% reduction in resin acids and 95% in fatty acids was reported from initial concentrations of 7.0 and 8.5 mg/L for resin and fatty acids respectively. This was done in a 1 m tall, 15 L column, with 400 mL/min air introduced via a tube and mixed with an impeller at 1700 rpm. It was concluded that flotation provided a practical and useful method for removing fatty and resin acids.

In 2002 Korpela reported successful lab-scale removal of wood resin from mechanical pine pulp by flotation [92]. Later, in 2006, his study of the mechanisms revealed that IAF of colloidal resin particles followed first order kinetics as do mineral and ink flotation [85]. However, unlike mineral and ink flotation, the attachment and stability of resin particles and bubbles was found to be driven by Brownian diffusion and surface forces rather than by large scale inertial forces and collision of particles. This is consistent with Deryagin's theory for contactless flotation of small particles [87]. Flotation of fibre particles was explained by physical entrainment [85].

In 2005 Negro et al. reported a DAF process optimised for removal of wood extractives from Kraft mill process water from *Eucalyptus globulus* wood [94]. 80% removal efficiency of extractives was reported.

The following year, DAF was reported for removal of pitch and galacturonic acids from TMP water by Saarimaa et al. [95]. Coagulants and flocculants were added to aggregate the substances for removal by DAF. This removed 90% of pitch at pH 5.

In 2010 Haapala et al. reported the results of a study of the removal of stickies, ink and wood extractives from a variety of paper machine process waters including water from TMP [96]. The method removed 50% of extractives from TMP water using no additives but relying on surface active components in the water to generate froth in an IAF cell.

Opedal et al. reported 80-90% removal efficiency for wood extractives from TMP process water in a laboratory DAF system using cationic polymers in 2011 [97]. A similar process

was trialled on a mill site in Sweden using water from a compressive pre-treatment of *P. abies* wood chips and achieved up to 76% removal of extractives [98].

In 2012 and 2014, Zasadowski et al. published results of studies into flotation of various contaminants from *P. abies* TMP water using an IAF cell [99-102]. Multiple additives and variables were investigated. Good removal of extractives was achieved using the cationic surfactant dodecyltrimethyl ammonium chloride (DTAC). The IAF cell was found to be more effective than a less turbulent cell that generated bubbles by the release of air through a glass frit at the base [100]. The effect of pH, calcium concentration, temperature, airflow and DTAC concentration on the IAF method were examined with the following conclusions. The method removed resin and fatty acids better than neutral extractives. Acidic pH was more effective than basic or neutral conditions with pH 5 found to better than 3.5 or 7.6 [99]. Removal of extractives was reduced by increased calcium concentration, and improved by higher airflow or a higher temperature of 50°C compared to 20°C. Increased DTAC concentration improved flotation but also increased the foam volume and water lost with the foam. The highest removal reported was a 92% reduction in extractives concentration.

1.7 Aims of the project

It is apparent from the literature reviewed, that wood extractives have useful properties and value as a natural product with future markets expected to expand. Removal of wood extractives has been reported to be beneficial to TMP mills reducing the problems caused by wood extractives in process circuits and wastewaters. There is also evidence that a flotation method may be a feasible way to remove wood extractives from process waters.

There has, to date, been no published literature demonstrating the recovery of wood extractives after removal by flotation. There is also very little research reported on flotation of wood extractives from *P. radiata* which has a different composition to the more commonly researched *P. abies* from the northern hemisphere. The higher proportion of resin acids in *P. radiata* wood extractives is likely to produce colloids with different surface chemistry and potentially different flotation behaviour. The mechanism of flotation of wood extractives is not well understood and there have been very few insights in this area. The research that has been published, suggests that the mechanism is different from that involved in the more

established flotation of minerals and flotation deinking. An understanding of the flotation mechanism is important for the development of a reliable flotation method. Implementation, of such a method would benefit the pulp and paper industry by reducing process problems caused by wood extractives, allowing for increased water saving, reduction in waste and production of a valuable natural product.

This project will address these gaps. It will:

1. Develop a reproducible lab scale flotation method for removal of *P. radiata* wood extractives from TMP process water.
2. Investigate the effect of process variables to optimise flotation of extractives and understand flotation mechanisms.
3. Investigate the influence of process water characteristics on flotation.
4. Investigate methods to recover extractives and additives from the flotation process.

Chapter 2 Materials and Methods

2.1 Flotation cell

Flotation was performed using a Denver D12 laboratory flotation machine (Figure 2-1). During the flotation method development process, additional equipment was introduced to the cell which consisted of:

1. a custom built five litre cylindrical stainless steel flotation vessel.
2. a temperature controlled water bath (Lauda element, thermostat and pump) surrounding the flotation vessel.
3. a rotameter (MPB Industries) for measurement of airflow through the air inlet.
4. a vacuum pump (Vacuubrand diaphragm pump) and Buchner flask for collection of froth.

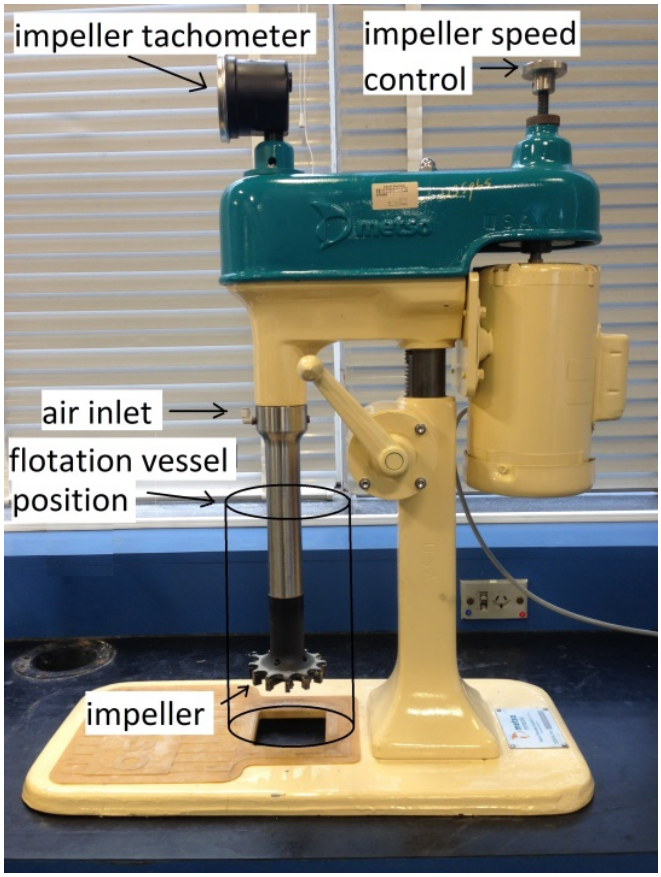


Figure 2-1 Denver D12 laboratory flotation machine

2.2 Flotation method

Flotation was performed on one litre batches containing 975 mL of process water. The total volume was made up with surfactant solution and deionised water as required, with HCl (RCI Labscan) or NaOH (Chem-Supply) added for pH adjustment. Calcium chloride (Chem-Supply) or sodium chloride (Merck) were also added when studying the effect of ionic strength. The water was sampled in duplicate before flotation. During flotation, the froth was collected from the solution surface at 2 min intervals using a vacuum pump (Vacuubrand diaphragm pump), Buchner flask and hose. Temperature, airflow and impeller speed were controlled. The volume of collapsed froth liquid collected was recorded along with the remaining volume of process water. The treated process water was sampled in duplicate.

2.3 Quantification of flotation efficiency

Flotation efficiency was reported as a percentage reduction in extractives concentration by the flotation process. It was calculated from the initial concentration (i) and final concentration (f):

$$\text{Flotation efficiency, F (\%)} = \frac{i-f}{i} \times 100 \qquad \text{[Equation 8]}$$

$$= \left(1 - \frac{f}{i}\right) \times 100 \qquad \text{[Equation 9]}$$

Duplicate samples were taken before and after each flotation treatment generating two values for both i and f. The mean of each duplicate was used to calculate F. The pre-flotation water with concentration i, included the addition of surfactant and/or pH adjustment which diluted it to 97.5% of the original process water concentration. Flotation efficiency was calculated for each class of extractives: fatty acids, resin acids and triglycerides as well as the total extractives which combined all three.

To quantify the uncertainty in F, the minimum and maximum (F_{min} and F_{max}) were calculated as given in Equations 10 and 11 below using the minimum and maximum values of i and f. F_{min} and F_{max} were then plotted as error bars to indicate uncertainty in the figures.

$$F_{max} = (1 - \frac{f_{min}}{i_{max}}) \times 100 \qquad \text{[Equation 10]}$$

$$F_{min} = (1 - \frac{f_{max}}{i_{min}}) \times 100 \qquad \text{[Equation 11]}$$

In addition to the flotation efficiency, the volume of water lost as a component of the froth was reported. This was important as it determined the concentration of extractives in the froth and the volume of treated water that would be available for recirculation.

2.4 Process water and characterisation methods

Process water was collected in 10 – 30 litre batches as required from one of four process streams at the Boyer and Albury pulp and paper mills. Each batch was characterised by a series of tests and kept refrigerated in a closed container at 4 °C for a maximum of 5 weeks. The water was then discarded for a fresh batch. This was done to avoid any changes that could result from the growth of microorganisms or decomposition of materials.

Each batch of water was sampled in duplicate or triplicate, depending on the batch volume, and the tests described below performed on each sample. Characterisation results for each batch of process water are provided in Appendix B.

pH

A handheld pH meter (TPS Aqua-pH) with temperature correction probe was used to measure the pH. The pH meter was calibrated weekly against pH 4.0 and pH 7.0 standard solutions (TPS).

Conductivity

A handheld conductivity meter (Hanna HI 8733) was used to measure conductivity. This was calibrated before each use using a commercial conductivity standard solution (HI 70030).

Calcium

Calcium concentration was determined by titration with ethylenediaminetetraacetic acid (EDTA) (Univar) according to a standard method for water analysis [103].

Soluble carbohydrates

Soluble carbohydrates were determined by a spectrophotometric method used at Norske Skog based on a published method[104]. Samples were quantified against a calibration curve plotted from standard glucose solutions (10, 30, 60 and 100 mg/L) and a deionised water blank which were prepared fresh and processed along-side the samples. Orcinol reagent was prepared by mixing 0.2 g of orcinol monohydrate (Sigma Aldrich) with 100 mL of concentrated sulphuric acid (Scharlau). Samples were filtered through 0.45 µm cellulose acetate (Maine manufacturing), diluted appropriately, and 1 mL mixed with 2 mL of orcinol reagent in teflon tubes. The tubes were capped, shaken and put in a water bath at 80 ºC for 15 min, then cooled on ice and the absorbance at 540 nm was measured using a Milton Roy Spectronic 20D UV/Vis spectrophotometer.

Fibre

Fibre content was determined from the weight of the total suspended solids by filtration through Whatman #541 filter paper and drying at 60 °C until constant weight.

Wood extractives

Three different portions of each sample were taken in order to quantify the dissolved, fibre-bound and colloidal extractives. The first portion was taken neat to quantify total extractives. Then the sample was centrifuged at 500 G for 10 min using an Eppendorf 5810 centrifuge to settle out the fibre-bound extractives and a second portion was taken from the supernatant liquid. This liquid was then filtered through 0.45 µm cellulose acetate (Maine manufacturing) to remove colloidal material giving the third portion containing only the dissolved extractives. The samples were then analysed by gas chromatography by the method described in the following section

2.5 Wood extractive analysis by gas chromatography

The method used for quantitation of wood extractives in water was based on a method previously established and used in industry[50, 105].

Standards

An external standard was prepared containing oleic acid (≥99% Fluka), dehydroabietic acid (99%+ CanSyn Chem. Corp.) and triolein (≥99% Sigma) in toluene. This was used to determine relative response factors which were applied to fatty acid, resin acid and triglyceride components respectively. An internal standard contained heptadecanoic acid (≥98% Sigma) for quantification and cholesteryl stearate (99% Sigma) and glyceryl triheptadecanoate (~99% Sigma) for extraction recovery corrections.

Sample preparation

1. The sample for analysis was diluted appropriately and 5 mL transferred to a 10 mL glass centrifuge tube.
2. The pH was adjusted to 3.5 using dilute nitric acid and pH test strips. 100 µL of internal standard was added using a 500 µL syringe.
3. 2 mL of MTBE was added.
4. The tube was capped and shaken for one minute.
5. The sample was centrifuged for 10 minutes at 500 G in an Eppendorf 5810 centrifuge.
6. The top MTBE layer was transferred by Pasteur pipette to a 2 mL GC vial and evaporated under air.
7. 1.7 mL of MTBE was added to the tube for a second extraction.
8. Steps 4-6 were repeated

The sample was redissolved in 1 mL of toluene.

Gas chromatography

Samples were analysed using a Varian CP-3800 GC-FID with CP-8400 auto sampler and CP-1079 injector. A Phenomenex© 100% polydimethylsiloxane (ZB-1, L = 15 m, I.D. = 0.53 mm, df = 0.15 µm) ZebronTM capillary GC column was used with helium mobile phase at a constant pressure of 6 psi. Samples were injected on-column with an initial injector temperature of 100 °C which was held for 0.5 min then ramped up to 325 °C at a rate of 180 °C min^{-1} and maintained for 28.3 min. The initial column oven temperature of 100 °C was

maintained for 2 min then ramped up to 320 °C at a rate of 15 °C min^{-1} and held constant for 13.3 min.

Quantitation

Peaks were identified based on their order of elution and by comparison with elution times for known standards of stearic acid (Aldrich), linoleic acid (Aldrich), neoabietic acid (Orchid Cellmark), abietic acid (CanSyn Chem. Corp.), pimaric acid (Abcam) and isopimaric acid (Helix Biotech). Peak areas were integrated using Varian Star software. The concentration in each sample was calculated by comparison with the heptadecanoic acid peak in the internal standard, taking into account the relative response factor obtained for each class of compounds (fatty acids, resin acids and triglycerides) using the external standard. A correction factor was also applied to account for extraction recovery efficiency during the sample preparation. This correction factor was based on recovery of cholesteryl stearate and glyceryl triheptadecanoate in the internal standard for each injection. The cholesteryl stearate recovery was used to correct fatty and resin acid concentrations and the glyceryl triheptadecanoate recovery was used to correct the triglyceride concentrations.

Figure 2-2 shows example chromatograms of the external standard and a process water sample with internal standard obtained by this method. Peaks were quantified individually and then combined to give total extractives concentration as well as fatty acid, resin acid, and triglyceride subtotals.

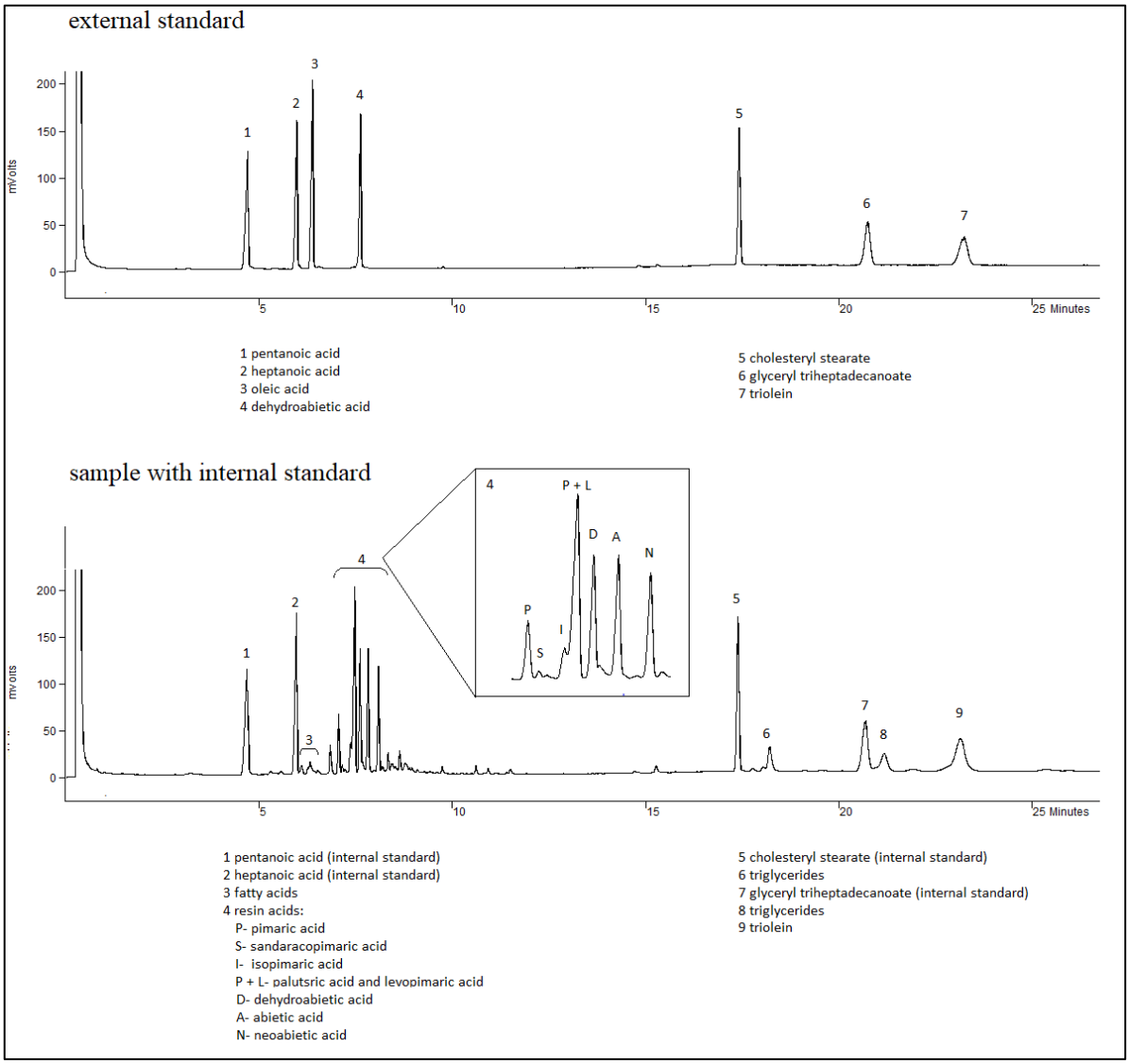


Figure 2-2 Example chromatograms of the external standard and a process water sample with internal standard added

2.6 Fibre length measurements

A Metso FiberLab automated optical measurement system was used to determine fibre length distributions. Results were acquired using FiberLab software then graphed in Microsoft Excel. For each sample, between 8 and 20 thousand individual fibre particles were measured. These length measurements were then used to plot a population distribution by calculating the percentage of total measurements within each 0.05 mm interval of fibre length.

2.7 Zeta potential measurements

Zeta potentials of wood extractive colloids were measured using a Malvern Zetasizer Nano and a DTS1070 cell at 25 °C. Results were modelled using Malvern software as protein in water using the Smoluchowski model.

The wood extractive colloids were obtained from process water sampled from Screwpress 2 on 16-Dec-2014. The process water was centrifuged at 500 G for 10 min using an Eppendorf 5810 centrifuge to remove fibre. The supernatant was used for zeta potential measurements with addition of NaOH (Chem-Supply) or HCl (RCI Labscan) for pH adjustment. Measurements were made on samples containing 80 mg/L dodecyltrimethyl ammonium bromide (DTAB) and on samples with no added surfactant.

2.8 DTAB analysis by UPLC-MS

This method was developed by Assoc Prof Noel Davies, Central Science Laboratory (CSL), University of Tasmania, for this project and all analyses using the method were done by either Noel Davies or David Nichols at the CSL.

Samples were analysed using a Waters Acquity H-series UPLC coupled to a Waters Xevo triple quadrupole mass spectrometer. A Waters Acquity UPLC BEH C18 column (2.1 x 100mm x 1.7 µm particles) was used, with mobile phases A = 1% acetic acid in water and B = acetonitrile. A linear solvent gradient from 55% A: 45% B to 25% A: 75% B over 2.5 minutes was used followed by 3 minutes re-equilibration time. Flow rate was 0.35 mL/min and the column as held at 45 °C. The mass spectrometer was operated in positive ion electrospray mode and DTAB was targeted by Multiple Reaction Monitoring (MRM). The ion source temperature was 150 °C, the desolvation gas was nitrogen at 1000 L/hr, the desolvation temperature was 300 °C and the capillary voltage was 2.7 KV.

MRM transitions for DTAB were (m/z) 228.3 to 60.1 and (m/z) 228.3 to 57.1 with the former used for quantitation. Cone voltages were 28 V and collision energies were 26 V. MRM transitions for hexadecyltrimethylammonium bromide (CTAB) internal standard were (m/z)

284.3 to 60.1 and (m/z) 284.3 to 57.1 with the former used for quantitation. Cone voltages were 40 V, collision energies were 26 V and dwell times were 78 ms per channel.

Where possible, CTAB was added as an internal standard to samples at 5 ppm and used for quantitation. Where this was not possible, reference standard solutions of DTAB were run at 10, 5.0, 2.0, 1.0, 0.5 and 0.1 ppm levels to create an external standard calibration, which gave a quadratic fit with correlation coefficient of 0.9951.

Data were acquired and processed with Waters MassLynx and TargetLynx software.

2.9 Preparation of dissolved organic wood polymers

The dissolved organic wood polymers were prepared by Dr. Karen Stack based on a method published by Orso et al. [106]. Lipophilic wood extractives were first removed from *P. radiata* TMP by Soxhlet extraction with hexane. The pulp was then disintegrated in water to 2% consistency at 60 °C for 3 h and then filtered. The filtrate was used to dilute more pulp and repeat the extraction process. This procedure was repeated up to 5 times to concentrate the filtrate which was then filtered through 0.45 µm filter paper to obtain the dissolved organic wood polymers. This dispersion was dialysed for 24 h in 1 mM KCl with pH adjusted to 5.5 to remove impurities using a cellulose membrane tubing (Sigma D-9402, 76 mm wide, >12,000 MW).

2.10 Ultra-filtration

Ultra-filtration was performed using a 450mL UHP-76 MFS stirred cell by Advantec. Filters used were Millipore regenerated cellulose YM3 NMWL 3000.

2.11 Solvent extraction of wood resins from froth

Duplicate samples of about 25 mL of froth concentrate solution were taken for each variable. These samples were weighed using an A&D electronic balance into 50 mL polypropylene centrifuge tubes. The pH was adjusted if necessary using sodium hydroxide (Chem-Supply) or hydrochloric acid (RCI Labscan). 10 mL of solvent was added. Solvents investigated included n-hexane (VWR Chemicals HiPerSolv Chromanorm 95%), n-heptane (Sharlau 99%

HPLC grade), toluene (Sigma Aldrich, chromasolv 99.9%), methyl tert-butyl ether (MTBE)(Chromasolv), and ethyl acetate (Chem-Supply). The centrifuge tubes were capped and shaken vigorously for 1 min before centrifugation for 10 min at 500 G using an Eppendorf centrifuge 5810. The solvent layer was then removed using a Pasteur pipette and transferred to a pre-weighed sample vial. A second extraction was performed by repeating the 10 mL solvent addition, shaking and centrifugation. The solvent layer was again removed and added to the sample vial. The solvent was then evaporated from the extract at room temperature. The extract was weighed to obtain the final weight, then redissolved in toluene with added internal standard for GC analysis.

Chapter 3 Flotation method development

3.1 Introduction

It was necessary to develop a reproducible method for studying flotation of wood extractives from *P. radiata* TMP process water. This involved the selection of a flotation cell, measurement equipment, process water source, additives to aid flotation and a method for quantifying the flotation efficiency.

The available literature on flotation of wood extractives includes foam fractionation, DAF and IAF methods. Promising results have been reported on IAF removal of extractives from TMP process water, including Zasadowski's favourable comparison of a 6 L Voith cell to a custom built 1 L cylindrical cell in which nitrogen was introduced through a sintered glass base [85, 96, 100]. These accounts were the basis for the selection of IAF as a method for this study. A Denver D-12 flotation cell was chosen for its benchtop size. However, being built for mineral flotation applications, some changes were necessary to adapt it to flotation of wood extractives. A different shaped flotation vessel and a different froth collection method were devised which reduced the amount of water removed as a component of the froth. This is important in wood extractive flotation where the aim is to separate extractives from process water, whereas it is not important in mineral flotation where the aim is to separate minerals from impurities and water is used merely as the medium. Further additions to the flotation cell were made to measure airflow, and temperature which are known to be important to flotation. The three reported IAF methods for TMP process water are listed in Table 3-1. These methods give insight into which parameters are most important for developing and optimising a method for flotation of wood extractives and into methods for quantification of flotation efficiency.

Table 3-1 Literature detailing IAF of wood extractives

Authors	Year	Country	Water	Flotation cell	Reference
Korpela	2006	Finland	*P. abies* & *Pinus silvestris* TMP	15 L Outokumpu	[85]
Haapala et al.	2010	Finland	unspecified TMP	20 L Voith	[96]
Zasadowski et al.	2012	Sweden	*P. abies* TMP	6L Voith	[100]
Strand et al.	2012	Finland	*P. abies* TMP	6L Voith	[99]
Zasadowski et al.	2014	Sweden	*P. abies* TMP	6L Voith	[102]

Korpela used a 15 L Outokumpu flotation cell to remove extractives from *Pinus silvestris* and *P. abies* TMP and study the mechanism of flotation of extractives and fibre [85]. The pulp was suspended in water with addition of $CaCl_2$ and had a pH around 5. Flotation was performed at 50 °C, with an airflow of 6 L/min and impeller speed of 2400 rpm. Froth was removed manually using a plastic scraper and a constant solution level was maintained by addition of deionised water. It was reported that fibre was floated by entrainment and resin colloids by contactless flotation. The enhancement of extractives flotation by addition of $CaCl_2$ was attributed to a combination of three influences: reduction in zeta potentials due to the increased electrolyte concentration leading to stronger bubble-colloid attachment, possible reduction in bubble size, and stabilisation of the froth. Addition of calcium ions is known to affect fatty acid monolayers by binding to carboxylate groups resulting in ordering and stiffening of the layer [107]. This effect may contribute to the alteration of flotation. Resin removal was reported by Korpela as a percentage and water loss and fibre loss were also measured. Resin particles were found to agglomerate in the froth which was attributed to their proximity after drainage and collapse of the froth.

Haapala et al. used a 20 L Voith Delta25 cell to remove extractives from deinked pulp and TMP whitewater [96]. The focus was on selective removal of contaminants from the total solids without chemical additives. Loss of water in the froth was not measured. The TMP whitewater was from unspecified northern hemisphere species and had a pH of 4.2. Flotation was performed at 45 °C with airflow of 7.4 L/s for up to 5 min. Froth was continuously removed and a constant solution level was maintained by addition of whitewater. The extractives removal was reported as a percentage reduction in concentration. The yield of total solids (percentage remaining in the treated water) was also measured and a selectivity index for each class of extractives was calculated. Non-polar triglycerides and sterols were

removed more selectively than fatty acids and resin acids. A 50% reduction in extractives with 70% yield was reported.

Zasadowski et al. used a 6 L Voith cell to study flotation of extractives and manganese ions from *P. abies* TMP process water [100]. A variety of foaming agents were tested as flotation additives and the cationic docecyltrimethylammonium chloride (DTAC) was found to be the most effective. This was attributed to greater interaction with the negatively charged wood extractive colloids due to the positive charge on the foaming agent. The Voith cell was also found to be more effective than a custom built 1 L cylindrical cell in which nitrogen was introduced through a sintered glass base. Equivalent removal of extractives was achieved in the Voith cell with shorter flotation times and less foaming agent compared to the custom cell. This was attributed to greater turbulence in the Voith cell. Flotation was also found to affect the fibre profile in the process water, with a shorter average fibre length found after flotation. This was attributed to fibres being cut by the impeller action in the Voith cell. In subsequent publications, the effect of various parameters on flotation were investigated [99, 102]. These included pH, temperature, DTAC concentration, airflow and calcium concentration.

Based on this research, it was necessary to measure and control the pH, temperature, airflow, impeller speed. A method for quantifying flotation efficiency was also necessary.

3.2 Results and Discussion

3.2.1 Process water and the effect of pH and fibre content

An initial consideration was the choice of process water to use for studying flotation of wood extractives. The possibilities included model process water made up from either wood extracts or pure compounds, or process water taken from various process streams at Norske Skog's Boyer mill. The main advantage of model process water would be that it could be made up consistently with a known composition. However, it is difficult to accurately model real process water which contains a variety of components that affect colloid behaviour and are likely to also affect flotation. It was therefore decided to work with process water

collected from the mill. The disadvantages in this choice include: the unknown composition, batch to batch variability, and limited shelf life of the process water. These were addressed by characterising each batch of water collected followed by storage under refrigeration at 4 °C for a maximum of 5 weeks. Details of characterisation are given in Chapter 2.4.

The process stream initially chosen for flotation studies was called Screwpress 2 and captured water immediately after the pulping stage where the wood extractives are released, making it an appropriate point to remove extractives before circulation to other mill processes. This process water was used to study the effect of pH and fibre content on flotation. First, the effect of pH on the proportions of extractives in the dissolved, colloidal and fibre-bound phases was investigated. The results are presented in Table 3-2. The initial pH of the process water was 5.18 and the fibre content was 0.36%. The concentrations of aluminium and calcium ions were not measured directly in that particular batch but are estimated from the average calcium concentration recorded for the Screwpress 2 process stream to be around 40 mg/L (refer to Appendix B for characterisation results). Soluble aluminium in the process water is very low, likely less than 0.01 mg/L. A possible source of aluminium is from aluminium sulfate which is added as a coagulant during raw water treatment, but this is expected to precipitate entirely as alum flocs which are settled and removed prior to the treated water entering the process.

Table 3-2 Phase distribution of wood extractives at different pH in TMP process water (Screwpress 2, 14/04/2014)

Extractives class and total concentration	**pH**	**dissolved**	**colloidal**	**fibre bound**
fatty acids 16 ± 1 mg/L	pH 3	13%	82%	5%
	pH 5	13%	69%	17%
	pH 8	18%	76%	6%
resin acids 250 ± 10 mg/L	pH 3	2%	67%	31%
	pH 5	4%	64%	32%
	pH 8	17%	56%	27%
triglycerides 122 ± 2 mg/L	pH 3	1%	93%	6%
	pH 5	2%	94%	4%
	pH 8	1%	90%	9%

Across the range of pH 3 - 8 studied, most extractives were in the colloidal phase which emphasises the importance of a focus on this phase for removal by flotation. However, the percentage of extractives in the colloidal phase dropped with increasing pH. This drop was most significant for resin acids and least for triglycerides. Resin and fatty acids in the dissolved phase increased with pH as expected due to deprotonation of the carboxylic acid group which increases the water solubility. The concentrations in the dissolved phase were higher than literature values for solubility of resin acids which range from 1-5 mg/L [9] and fatty acids which are less than 1 mg/L [14]. This may be due to the complex process water mixture compared to the purified water used for the literature values and also because the 0.45 µm filter used to separate the dissolved phase may allow through some sub 0.45 µm colloids and fibre particles. The study by Sundberg et al. in 2009 on pH and phase distribution of resin and fatty acids in wood pitch emulsions and TMP water found pK_{lw} values of around 5-7 for resin acids and around 7-11 for fatty acids [69]. The dissolved phase in the current study was found to be well below 50%. This could be largely due to the difference in resin and fatty acid concentration which is about ten times higher in the current study compared to that of Sundberg et al. As well as this, fibre was not present in the literature study. The percentage fatty and resin acids in the fibre bound phase was highest at pH 5 which was the original pH of the process water.

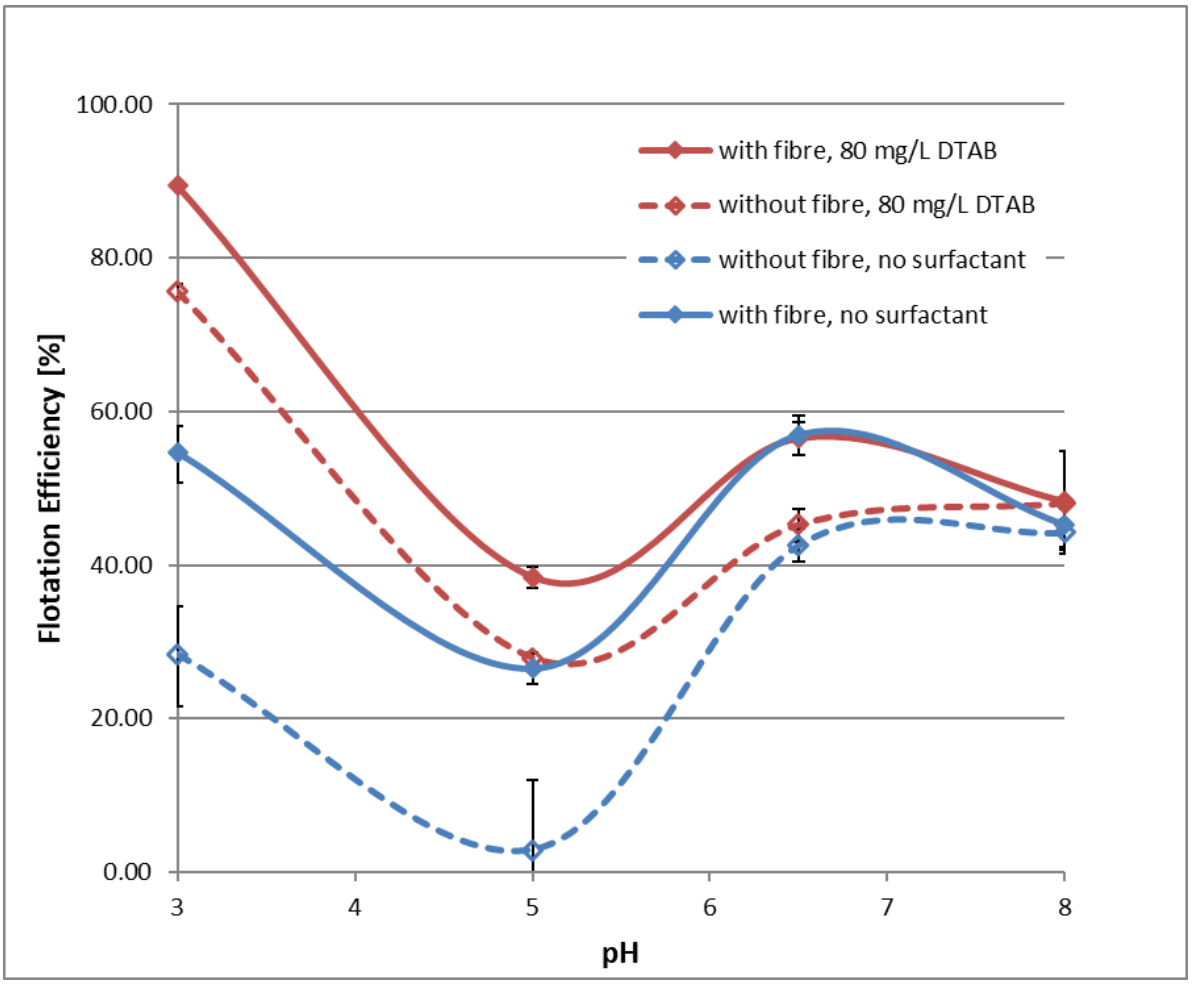


Figure 3-1 Effect of fibre content, pH and DTAB on flotation of wood extractives.

The fibre content of Screwpress 2 water was around 0.35 % and hindered interpretation of flotation results. The effect of fibre content was studied by pre-treating the process water (Screwpress 2, 14/11/2014) by centrifugation for 10 min at 500 G to remove suspended fibre particles. Flotation with this pre-treated water was then compared to flotation with process water without the pre-treatment. Flotation was performed with a preliminary method using 975 mL of process water, with pH adjusted to the values indicated in Figure 3-1, made up to 1 L, at 20 °C, in a 1.5 L rectangular flotation vessel. An impeller speed of 1300 rpm and airflow of 8.5 L/min were employed for 10 min. The removal efficiency was calculated from GC analysis of fatty acids, resin acids and triglycerides in the water before and after flotation. Those results, presented in Figure 3-1, show higher removal efficiency from process water with the fibre present, under all conditions except pH 8. Thus, the presence of fibre improved the flotation of wood extractives under these conditions. This improvement could be

explained by flotation of extractives with wood fibres either bound to the fibres or entrapped by them during flotation. At pH 8, the presence of fibre gave no significant improvement to flotation of extractives, and neither did the addition of DTAB suggesting a mechanism for flotation of extractives independent of these. At pH 8 there are more extractives in the dissolved phase and less in the colloidal and fibre bound phases (Table 3-2). Thus flotation at pH 8 may be mainly by adsorption of resin and fatty acid anions at the bubble surface rather than flotation of whole colloids or fibres.

Interestingly, the fibre content of the collected froth was between 0.2 and 0.3 % which was less than the 0.34 % content of the original process water (Table 3-3). This indicates that flotation did not greatly reduce the overall fibre content in the process water.

Table 3-3 Fibre content of froth collected during flotation (w/v %).

pH	3.0	5.0	6.5	8.0
80 mg/L DTAB	0.270 ± 0.003 %	0.234 ± 0.002 %	0.205 ± 0.009 %	0.220 ± 0.000 %
no surfactant	0.233 ± 0.003 %	0.287 ± 0.006 %	0.224 ± 0.002 %	0.268 ± 0.003 %

Original fibre content in the process water was 0.344 ± 0.006 %. Error is estimated standard deviation from the mean based on duplicate or triplicate measurements.

Visual inspection suggested that the longer fibres were collected in the froth and FibreLab analysis confirmed this (Figure 3-2). Analysis was performed on process water before and after flotation as well as on the froth collected. These samples were taken from flotations performed using a preliminary method which used 980 mL of process water (Screwpress 2, 11/09/2014) adjusted to pH 3.0, with 20 ppm added surfactant, and made up to 1 L. The flotation was then performed at 20 °C, in a 1.5 L rectangular flotation vessel, with 1300 rpm impeller speed and 8.5 L/min airflow for 15-60 sec to collect 50 g of froth. Figure 3-2 depicts the population distribution of fibre lengths in these samples. The distribution profile of fibre lengths contained in the original process water, shown in black, has a sharp peak around 0.2 mm and a mean fibre length of 0.53 mm. The treated water samples have very similar distributions, but the mean is slightly reduced to 0.51 mm for flotation without added surfactant and to 0.49 mm with DTAB. By contrast the profile for fibres in the froth collected

by flotation with DTAB has a broad peak and mean at 1.70 mm demonstrating selective flotation of the longer fibres. Froth collected with no added surfactant had a smaller shift toward longer fibre lengths with a mean of 0.82 mm.

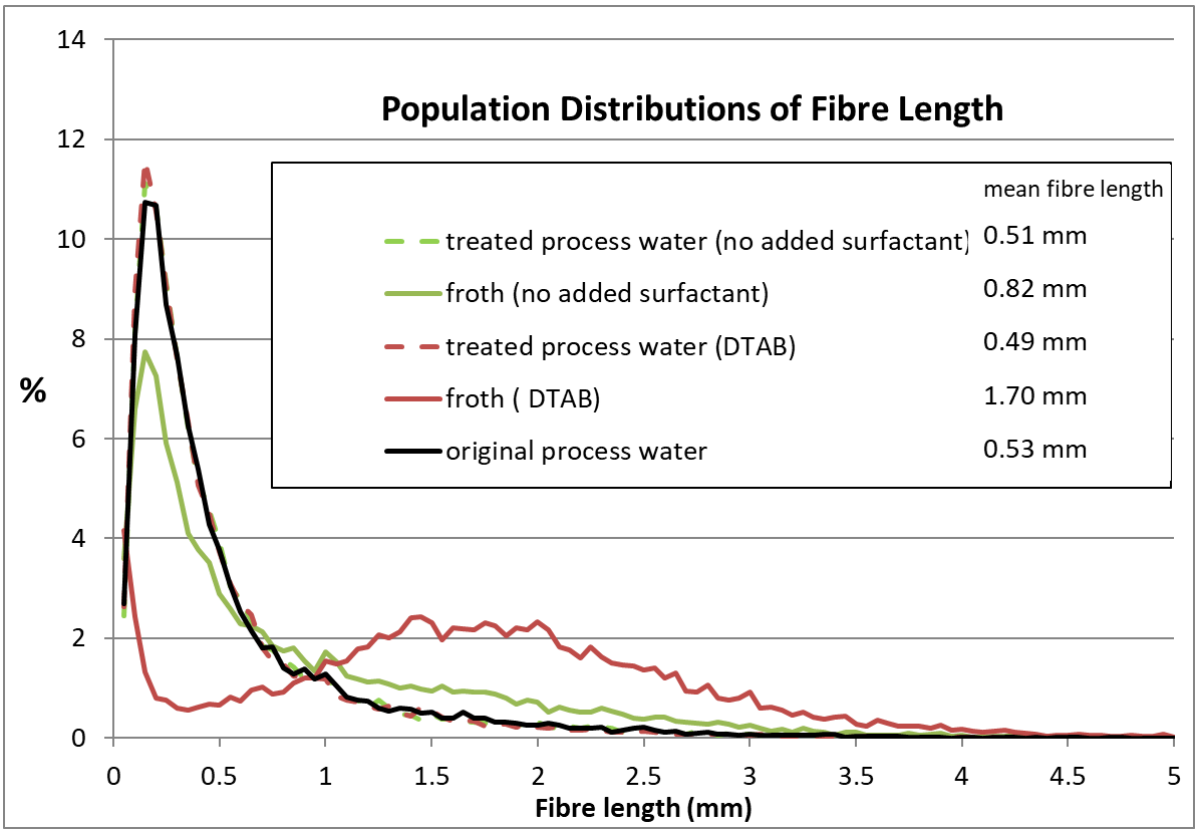


Figure 3-2 Fibre length in froth compared with fibre length in original process water

From this, it is concluded that flotation selectively removed longer fibres, and the cationic surfactant DTAB increased this selectivity. Removal of longer fibres resulted in a shift toward shorter fibres in the treated water. The mechanism for flotation of fibre is not clear but some possibilities can be contemplated. Longer fibres may be floated more easily by entrainment as they are less likely to drain from the froth. In terms of surface forces, longer fibres have more surface area for potential interaction with the bubble surface, but they also have greater weight and experience greater hydrodynamic forces due to turbulence that might dislodge the particle. The observed increase in selectivity of longer fibres with addition of DTAB suggests that surface chemistry plays a significant role, as does the change in fibre flotation with pH. There are several ways the surfactant might improve the attachment of fibres to bubbles. It might adsorb to the fibres as a collector or it might adsorb at the bubble

surface altering the surface charge. Most likely the mechanism for flotation of fibre is a combination of entrainment and electrostatic attraction between extractive anions on the fibre and cationic surfactant on the bubble surface.

The observed selective flotation of longer fibres combined with the observed improvement of extractives flotation in the presence of fibre suggests that the longer fibres either have higher extractives content or are better able to entrap colloidal extractives.

Analysis of the extractives content of different fibre fractions was attempted but proved problematic and inconclusive. The longer fibres in the floated fraction and the shorter fibres in the treated water were collected by filtration, but because this method also collected coagulated material, the results did not accurately reflect the fibre bound extractives.

Zasadowski et al. also observed a change in fibre length distribution after flotation treatment with DTAC [100]. The proportion of fibres in the 1.2 to 2 mm fraction was found to decrease from 17.2% to 5.2%, whereas the proportion in the 0.2 to 0.5 mm fraction increased from 27.8% to 42.9% during flotation. This represents a shift towards shorter fibre lengths as was observed in the current research. They also reported a reduction in the extractives content of fibres in the process water, from 42 200 mg/kg before flotation, to 16 700 mg/kg after. There was no reported analysis of fibres in the collected froth and the observed results were attributed to cutting of fibres by the impeller which released extractives for removal by flotation. However, in light of the current research, a plausible alternative explanation is proposed. The selective flotation of longer fibres and fibres with high extractive content would also lead to shorter average fibre lengths and lower extractives content in the fibres remaining in the process water. This could result in the observed shift in fibre length distribution and extractives content.

Flotation of fibre was not the primary aim of the current research and its interaction with the wood extractives complicated the interpretation of flotation results as it was difficult to differentiate the flotation of dissolved and colloidal extractives from those attached to fibre. Therefore, a different process stream was chosen for collection of process water. This stream captured water after a DAF fibre recovery process and was named DAF filtrate. This water had less than 0.1 % fibre content compared to around 0.35 % in the Screwpress 2 water.

3.2.2 Quantification of flotation efficiency

Various methods have been used by other researchers to quantify the efficiency of wood extractives flotation, with the method chosen depending on the objective of flotation. Research by Korpela focused on removal of extractives from pulp rather than from water, although the pulp was suspended in water for flotation [85]. Therefore, removal was quantified by the percentage of total extractives removed without concern for the water component [85]. Similarly, Haapala et al. removed extractives from process water with the focus on selective separation of the extractives from the solids [96]. Reduction in the concentration of extractives was reported, but the amount of water removed with the froth was not. Only Zasadowski et al. and Strand et al. have reported results in terms that fully quantified the water lost during flotation [99, 102]. They reported residual extractives in the treated water as a percentage of the initial concentration as well as collapsed foam volume [99, 102]. For the current research it was also important to quantify the water component, as the goal was to remove extractives from the bulk process water and produce a maximum volume of treated water for recirculation. Several methods of quantifying flotation efficiency of the batch-wise flotation process in the current study were considered.

The first was to simply calculate the weight of extractives in the batch of process water and report the percentage that was removed by flotation. However, this did not adequately quantify flotation efficiency because the loss in water volume with the froth was not accounted for. For example, removal of 50% of extractives where the water lost with the froth is also 50% is not selective flotation. The same result may be achieved by simply pouring out half the process water.

The enrichment of extractives in the froth was then considered and calculated as an enrichment factor relative to the initial process water. This proved to be difficult due to the high concentration and coagulation of extractives in the collapsed froth liquid. The high concentration necessitated dilution before measurement of extractives and the coagulation made accurate sampling and dilution difficult.

The chosen method was to report the flotation efficiency as a percent reduction in concentration of extractives in the final process water relative to the initial concentration. This was considered the most appropriate given that the goal of flotation was to reduce the concentration of extractives in process water. Reporting a relative reduction also enabled comparison between different extractive components and different batched despite variable initial concentrations.

The flotation efficiency (F) was calculated from the initial concentration (i) and final concentration (f) according to the following formula:

$$\text{Flotation efficiency, F (\%)} = \frac{i-f}{i} \times 100$$

$$= \left(1 - \frac{f}{i}\right) \times 100$$

It was still important to consider the water loss in addition to the removal efficiency as this determined the final volume of treated process water.

3.2.3 Airflow control

Airflow was expected to be an important factor in flotation, so it was necessary to measure and control the air entering the flotation cell. Air enters the Denver flotation cell via a channel in the impeller shaft. The air is drawn in by the impeller action alone with no external control. To measure the airflow, a rotameter flowmeter was attached at the air inlet. A depiction of the airflow through the flowmeter, impeller shaft and impeller is presented in Figure 3-3.

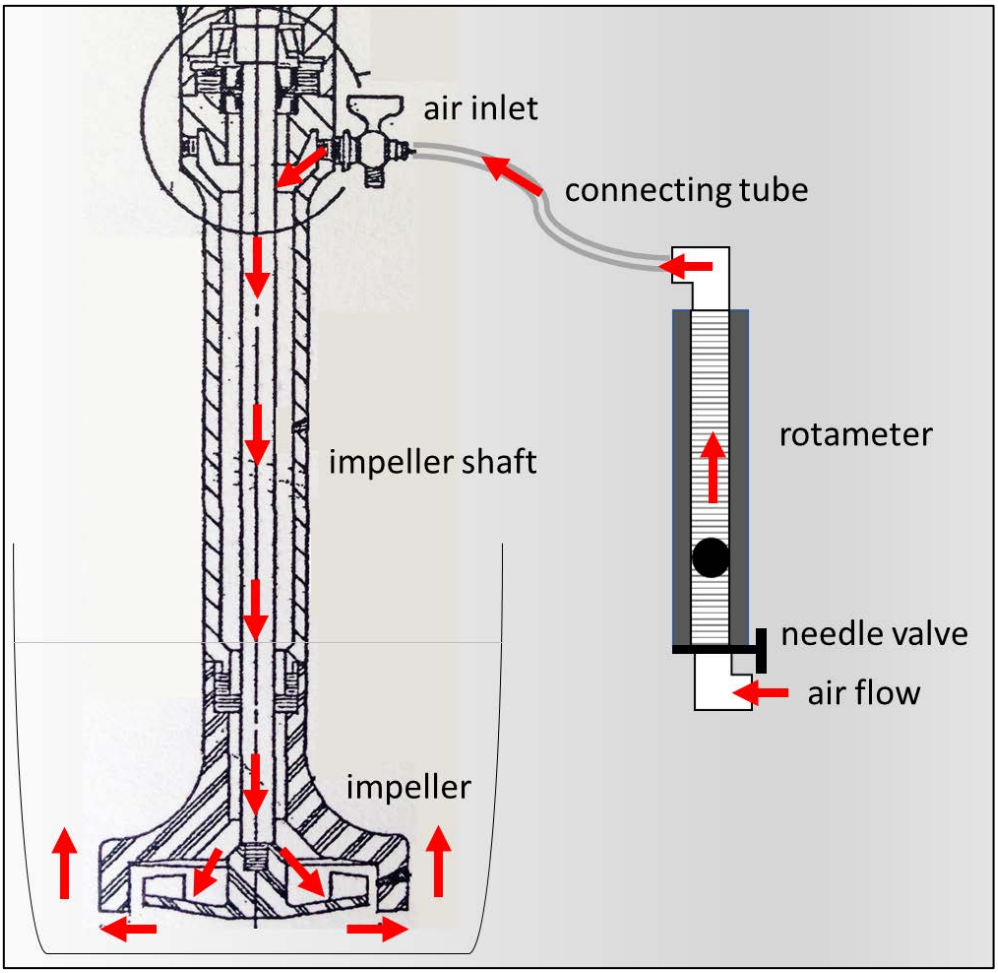


Figure 3-3 Air flow through the impeller shaft

The airflow was found to change depending on the length of the connecting tube. For example, 8.5 L/min was measured with a 29 cm connection whereas 4.5 L/min was measured with a 93 cm connection (both during operation at 1300 rpm impeller speed). Restriction of airflow with flowmeter attachment to an identical cell was also reported by Girgin et al.[108]. The longer connecting tube was more practical as it allowed the impeller to be raised and lowered so this length was retained. The airflow was also found to increase with impeller speed as shown in Figure 3-4. This is expected in an IAF cell [108]. The impeller tip speed was also calculated based on the rotor diameter of 70 mm. The effect of impeller speed and airflow on flotation efficiency is presented in Chapter 4.2.2.

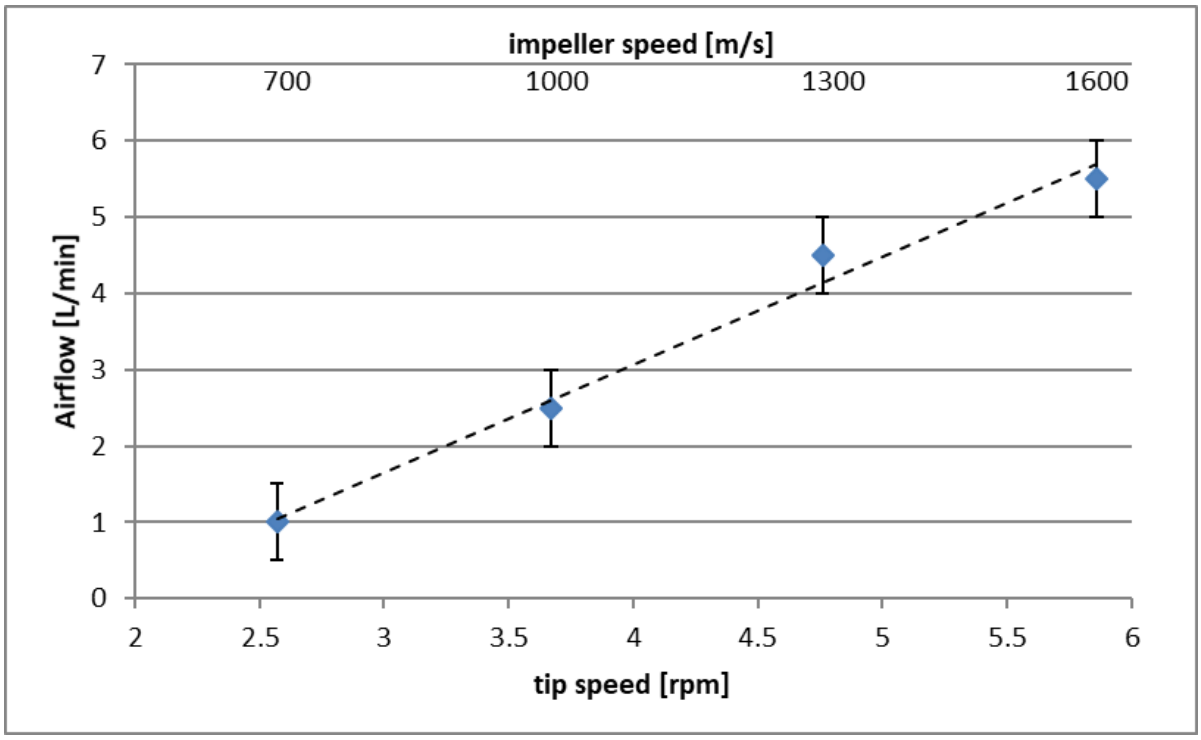


Figure 3-4 The effect of impeller speed on airflow. Using 1 L of water in the vessel and a rotameter attached to the air inlet. Error bars represent the fluctuation in airflow observed.

3.2.4 Flotation vessel and froth collection

The vessel supplied with the flotation cell was found to be unsuitable for flotation of wood extractives. This vessel was a 1.5 L rectangular tub with an overflow lip for collection of froth. However, the froth flowed so readily over the lip that an excessive volume of water was lost using this method. To remedy this, a taller cylindrical 5 L vessel was custom built. The two vessels are shown in Figure 3-5. The new vessel retained the water and allowed the froth to accumulate at the surface. The froth was collected during flotation from the vessel walls and mixture surface using a plastic scraper and a Buchner flask and hose connected to a vacuum pump.

Figure 3-5 Flotation vessels:the rectangular vessel supplied with the flotation cell and the custom made cylindrical vessel.

As displayed in Table 3-4, flotation with the new vessel resulted in a 78% reduction in the water lost during flotation with no reduction in the removal efficiency of wood extractives.

Table 3-4 Comparison of flotation vessels.

	old rectangular vessel	**new cylindrical vessel**	**change**
flotation efficiency	41.8 ± 0.6 %	41.4 ± 0.4 %	no change
water volume lost	385 ± 5 mL	85 ± 5 mL	78% reduction
Flotation parameters: pH 5, maximum airflow, 1300 rpm impeller speed, 20°C, 1 L volume, 80 mg/L DTAB, 10 min flotation time, process water from Screwpress 2, 16/12/2014 centrifuged.			

It was also found to be beneficial to allow the froth to build up by collecting it at intervals rather than continuous collection. This minimised water loss without reducing removal efficiency by allowing excess water to drain from the froth. A similar observation was made by Korpela who found that resin particles agglomerated after drainage and collapse of the

froth [85]. The accumulation of froth varied greatly with changes in flotation variables, particularly with foaming agent used and flotation time. However, a standard two minute interval time for froth collection was chosen as this was the minimum time that the froth height could reach the top of the flotation vessel.

3.2.5 Temperature control

It was necessary to control the temperature so that its effect on flotation could be studied. Simply heating the process water on a hotplate to the desired temperature before flotation was not sufficient because there was a significant drop in temperature during flotation. For example, after 20 min of flotation the temperature of 1 L of process water dropped from 50 °C to 40 °C. The heat was lost through the walls of the flotation vessel and to the air drawn through the mixture by the impeller which in this example was at a rate of 4.5 L/min. To maintain the temperature of the mixture during flotation, the vessel was placed in a temperature controlled water bath. This consisted of a plastic tub and a Lauda element, thermostat and pump. This effectively maintained the temperature over the range studied which was 20 to 70 °C. The effect of temperature on flotation efficiency is covered in Chapter 4.2.4.

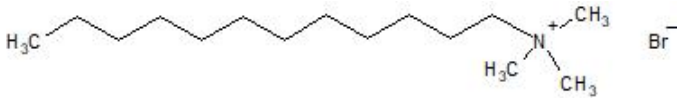
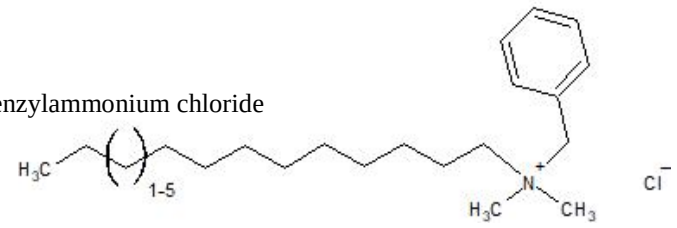
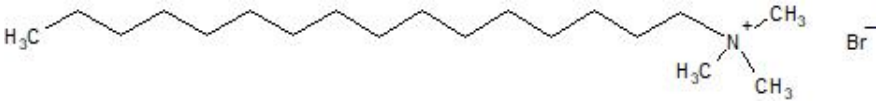
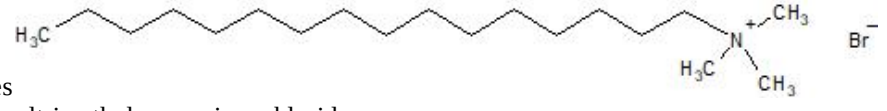
3.2.6 Comparison of surfactants

In mineral flotation, surfactant additives are categorised as either collectors or frothers depending on their role in enhancing flotation. A collector is added to alter the surface properties of mineral particles by adsorbing to the particle surface to make it hydrophobic and able to attach to air bubbles. A frother is added to alter the surface properties of the bubbles to promote bubble-particle attachment [79]. In practice, the system is complex and many surfactants are likely to alter the surface properties of both particles and bubbles and cannot necessarily be categorised neatly as either a collector or frother. Flotation of wood extractives can be achieved without added surfactants because the resin and fatty acids are themselves surfactants capable of generating a froth [85, 96]. However, the cationic surfactant DTAC has previously been shown to improve flotation [99, 100, 102].

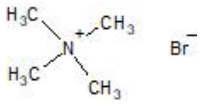
A variety of surfactant additives were tested to select the most effective foaming agent for flotation of wood extractives. These are listed in Table 3-5.

The quaternary ammonium surfactant DTAB was chosen based on the known improvement that could be achieved with DTAC, which is simply the chloride salt of the same cation [101, 102]. The change in anion should not alter its action. CTAB and TMAB were also tested to compare the effect of their differing chain lengths compared to DTAB. Quatramine 50 and 16/50 were included as they are industrial products containing similar quaternary ammonium surfactants. Sodium dodecyl sulphate (SDS) was tested as an example of an anionic surfactant, and Triton X-114 and X-100 as examples of industrial non-ionic surfactants.

Table 3-5 Surfactants investigated as foaming agents

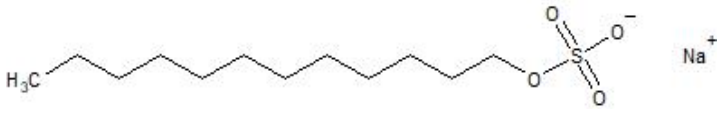
DTAB  class: cationic supplier: Acros Organics composition: 99% dodecyltrimethylammonium bromide cmc: 13-14 mM (~4g/L) [109, 110] concentration used 80 mg/L
Quatramine 50  class: cationic supplier: Nuplex Specialties composition: ~50% C12-C16 alkyldimethylbenzylammonium chloride Supplier: Nuplex Specialties cmc: 4-8 mM (~1.5-2.9 g/L) [109, 110] concentration used: 200 mg/L
CTAB  class: cationic supplier: Acros Organics composition: 99+% hexadecyltrimethylammonium bromide cmc: 0.7-1 mM (250-360 mg/L) [109, 110] concentration used: 80 mg/L
Quatramine 16/50  class: cationic supplier: Nuplex Specialties composition: ~50% hexadecyltrimethylammonium chloride cmc: 0.7-1 mM of active ingredient (250-360 mg/L) [109, 110] Concentration used: 200 mg/L

TMAB



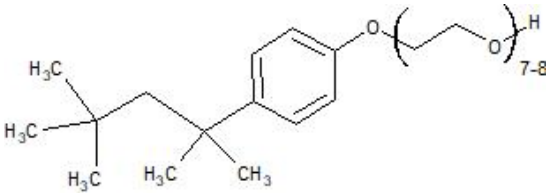
class: cationic non-surfactant
supplier: Acros Organics
composition: 98% tetramethylammonium bromide
concentration used: 80 mg/L

SDS



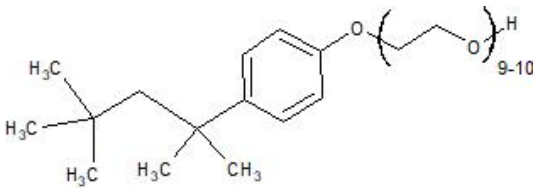
class: anionic
supplier: BDH
composition: 90% sodium dodecyl sulphate
cmc: 8.2 mM (2.4 g/L) [109]
concentration used: 80 mg/L

Triton X-114



class: non-ionic
supplier: BDH
composition: 60-100% (1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol
cmc: ~0.2 mM (~107 mg/L) [111]
concentration used: 80 mg/L

Triton X-100



class: non-ionic
supplier: BDH
composition: 60-100% (1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol
cmc: ~0.2 mM (~125 mg/L) [110, 112]
concentration used: 80 mg/L

Each foaming agent was tested by performing flotation treatment with addition of the foaming agent at the concentration listed in Table 3-5. The concentrations were selected to give around 80 mg/L of the active component which is below the cmc of each surfactant [109-111]. Flotation treatments were performed at three different pH values (3, 5 and 7) with each foaming agent, to compare its effectiveness across this range. Although the extremes of this range are not necessarily practical or representative of mill conditions, they were studied to give insight into the chemistry and mechanism of the flotation process.

Flotation results are shown in Figure 3-6 and Figure 3-7. They include the removal efficiency obtained with each additive at each pH value and that obtained with no additive (Figure 3-6), and the corresponding water lost during flotation, from an initial volume of 1000 mL of process water (Figure 3-7). The results show a clear difference between the classes of additives. Each of the cationic surfactants (red data points) improved the removal efficiency at the lower pH values of 3 and 5 with the maximum removal efficiency of 79% achieved using DTAB at pH 5. They also caused minimal water loss. The non-ionic surfactants (green data points) gave only limited improvement in removal efficiency at pH 5 and 7 accompanied by increased water loss. The anionic SDS (blue data points) gave improved removal efficiency at pH 3 and 7 but excessive water loss at every pH value. TMAB which is cationic but not surface active (purple data points), gave results very similar to those with no additive (black data points).

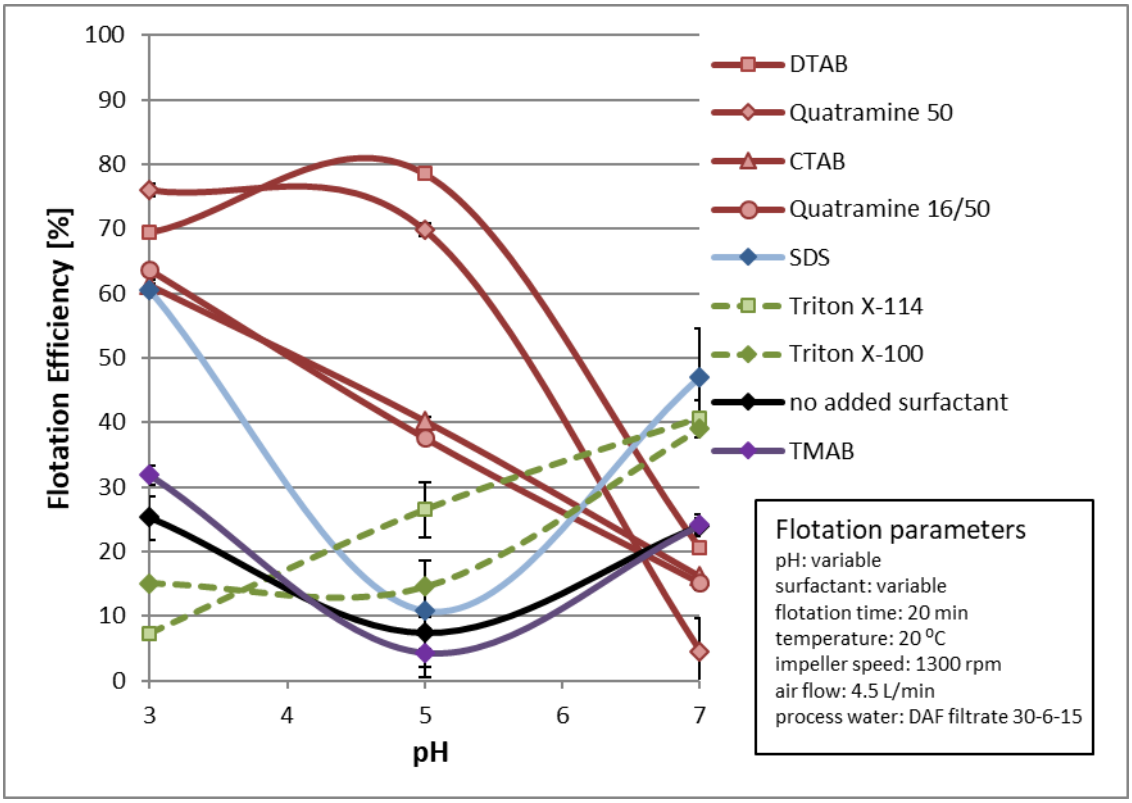


Figure 3-6 Flotation efficiency with different surfactants.

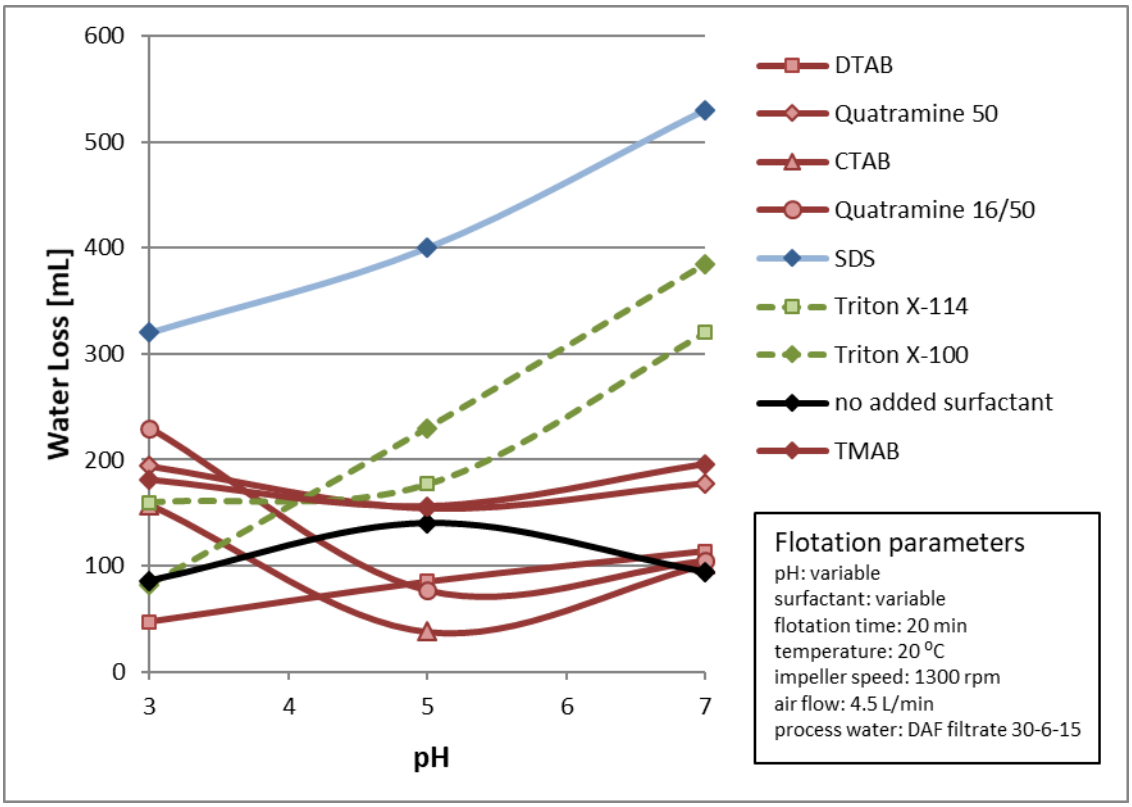


Figure 3-7 Water loss during flotation with different surfactants

To examine the possible flotation mechanisms that could explain these results, some additional information regarding surface charges needs to be considered. Figure 3-8 presents data on zeta potential measurements for wood extractive colloids and air bubbles over a pH range.

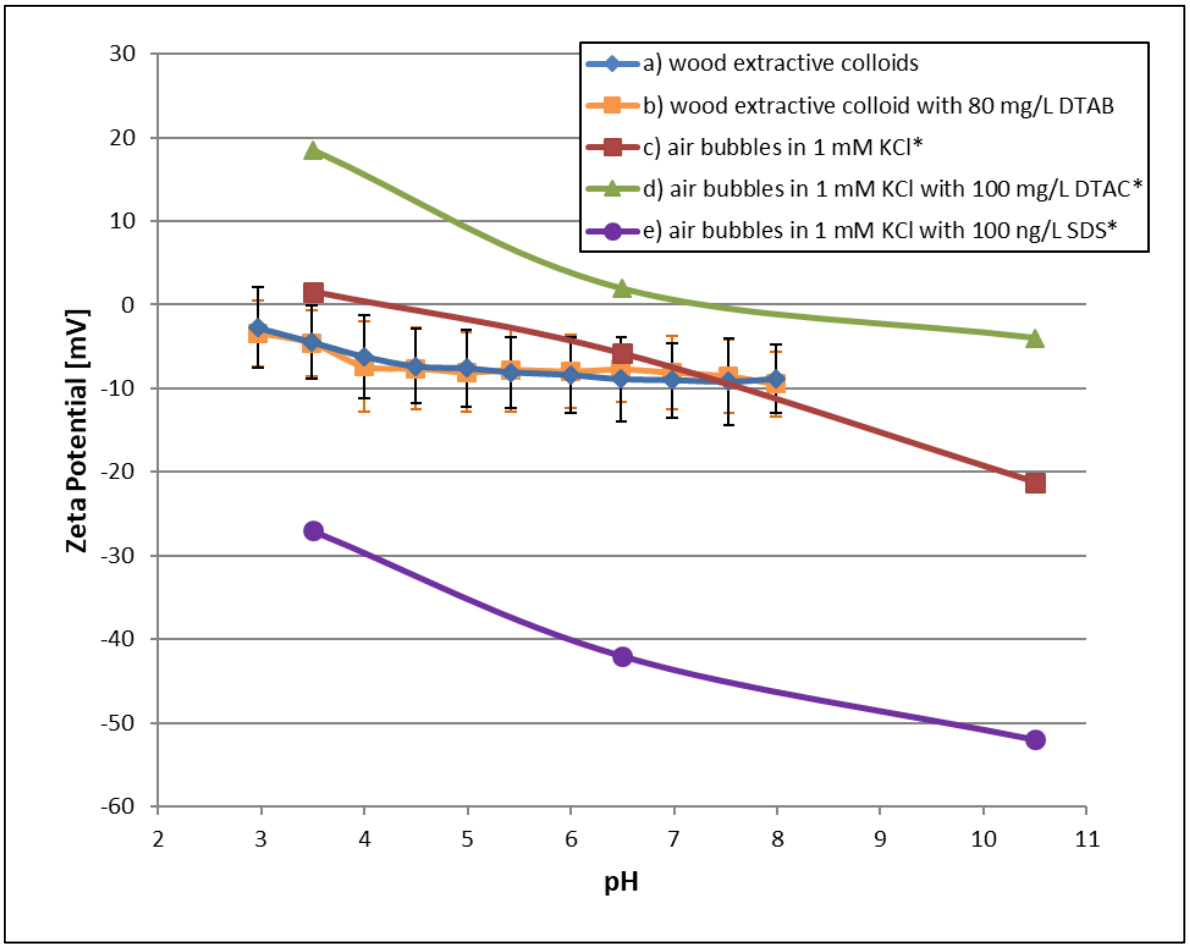


Figure 3-8 Effect of pH on zeta potential of wood extractive colloids and air bubbles. *data from work by Jia et al [113].

The blue trace (a) shows zeta potentials measured for wood extractive colloids in TMP process water. Although there was a range in zeta potential for the colloids (as shown by the error bars which represent standard deviation) the mean zeta potential clearly increased in magnitude with increasing pH from -2.72 mV at pH 3 to -8.87 mV at pH 8. An increase with pH was expected, due to deprotonation of resin and fatty acids at the colloid surface. The observed increase was steeper from pH 3 to pH 5 above which it increased only gradually, reaching a maximum (mean -9 mV) at pH 6.5. The steeper increase at pH 3-5 does not coincide with the pK_a of the wood extractives (around 7 for resin acids and 7-10 for fatty acids [12]) as might be expected. Rather the steeper increase might relate to changes in conductivity since HCl was added to alter the pH below pH 7 and NaOH above pH 7

resulting in higher conductivity between pH 3 and pH 5 (see Appendix C). The relatively consistent zeta potential on wood extractive colloids above pH 5 indicates little change in surface charge despite expected changes in deprotonation of resin and fatty acids. This may be because the anions generated enter the dissolved phase which is consistent with the work presented in Chapter 3.2.1 on phase distribution of extractives which showed a large increase in the dissolved resin and fatty acids between pH 5 and pH 8 (Table 3-2). Zeta potential measurements were also made for wood extractive colloids in process water with addition of 80 mg/L DTAB. These results are shown by the orange trace (b) in Figure 3-8. This trace is very similar to that without DTAB indicating that the DTAB did not interact significantly with the colloid surface to change its zeta potential as might have been expected due to their opposite charge. This could be because the monovalent charge on individual DTAB cations is effectively screened by electrolytes in solution.

The surface charge on air bubbles is also known to change with pH [113-115] and in the presence of surfactants [113]. At higher pH levels, an accumulation of OH^- is observed at air-water interfaces giving air bubbles a negative charge, whereas below around pH 2-4, the excess of H^+ ions in solution, result in a positive surface charge [113-115]. In Figure 3-8, zeta potential measurements reported by Jia et al. are presented. The red trace (c) shows the zeta potential of air bubbles in a weak electrolyte which is increasingly negative above pH 4. Anionic and cationic surfactants alter the surface charge because they adsorb to the air-water interface [113]. The green trace (d) shows that the addition of cationic surfactant DTAC shifts the zeta potentials to a net positive charge. The purple trace (e) shows that the addition of anionic surfactant SDS results in a negative shift in the zeta potentials. Jia et al. also showed that the magnitude of these zeta potential shifts increased with surfactant concentration [113].

Flotation efficiency without added surfactant was less than 10% at pH 5 but around 25% at both pH 3 and pH 7. The improvement at pH 7 can be explained by the increased ionisation and solubility of resin and fatty acids (having pK_a values around 7 and 7-10 respectively [12]) This enables them to adsorb as surfactants on air bubble surfaces and be removed during flotation. At pH 3 however, this is not the case, so there must be another mechanism operating. At pH 3 almost all extractives are protonated and in the colloidal phase, suggesting

flotation of whole colloids by attachment to air bubbles. This presumably occurs as a result of attractive surface forces since very small particles are unlikely to otherwise intercept air bubbles due to their low inertial force [80, 81]. Surface forces include van der Waals and electrostatic forces. The van der Waals interaction between air bubbles and colloids in water is expected to be repulsive as predicted by the effective Hamaker constant (see Equation 9, Chapter 1.4.4). Although exact values of Hamaker constants vary depending on methods for their calculation it can be surmised that $A_{air} < A_{water} < A_{extractives}$ [74, 75], thus the effective Hamaker constant will be negative implying repulsion. However, adsorption of surfactant species on bubble surfaces can reverse this [116, 117], but at low pH, with no added surfactant this would be unlikely. The electrostatic interaction is also expected to be repulsive over most of the pH range studied because the zeta potentials of both colloids and air bubbles are negative. However, with decreasing pH, these negative charges are reduced and below pH 4 the air bubble zeta potential becomes positive (as shown in Figure 3-8). Therefore, attachment may be favourable around pH 3 where air bubbles and colloids are oppositely charged. In summary, the proposed explanation is that flotation at the lower pH 3 occurred by colloidal flotation enabled by electrostatic attraction and at the higher pH 7 by surfactant flotation of dissolved extractives, whereas at pH 5 neither of these mechanisms occurred to a significant extent.

The addition of non-ionic surfactants resulted in flotation efficiency that increased with pH indicating surfactant flotation of dissolved extractives. The higher flotation efficiency at pH 5 and pH 7 compared to flotation without added surfactant may result from the increased foaming and hence increased bubble surface area for removal of extractives. Flotation efficiency at pH 3 was reduced by addition of the non-ionic surfactants. This is interpreted as a reduction in colloid flotation presumably by decreasing attractive surface forces but the exact mechanism for this is unclear. Adsorption of the neutral surfactant at bubble surfaces would not be expected to alter the electrostatic interaction with colloids. It would however be expected to result in an attractive van der Waals interaction [116, 117] though this should lead to improved flotation.

Flotation with addition of the anionic SDS gave a similar though exaggerated trend compared to flotation without surfactant and the explanations may be the same. A minimum in flotation

efficiency at pH 5 was observed with improved flotation at pH 3 and pH 7. The higher flotation efficiencies compared to those without added surfactant may be due to the increased foaming with SDS and increased bubble surface area for removal of extractives. Flotation at pH 7 as explained earlier, is likely to occur by surfactant flotation of dissolved extractives. This would involve competition with the more hydrophobic SDS for bubble surface area. However, as the surface area was very high due to the foaming ability of SDS, as evidenced by the high water loss (Figure 3-7), this may not inhibit adsorption of dissolved extractives. Furthermore, the SDS concentration would decrease during flotation as the foam was collected. At pH 3 colloidal flotation is more likely. With the addition of SDS, bubble surfaces should be more negatively charged and might be expected to reduce colloidal flotation at pH 3 which was not the case. However, addition of the ionic species would also raise the electrolyte concentration and compress the electric double layer around colloids and bubble surfaces reducing the range of electrostatic repulsion. The van der Waals interaction between bubbles and colloids should also become attractive with adsorption of surfactant [116, 117]. The net result of these changes could produce deeper primary and secondary minima and reduced energy barrier in the interaction energy which could enable flotation of colloids by attachment in the primary or secondary minimum.

The improved flotation with cationic surfactants agrees with the work of Zasadowski et al. who found DTAC improved flotation of wood extractives [99, 100, 102]. They also found that flotation was more efficient at pH 5.1 compared to 3.5 or 7.6 which is consistent with the current study which gave higher flotation efficiency at pH 5 compared to pH 3 and 7 (Figure 3-6). Cationic surfactants may influence colloidal flotation by two separate mechanisms which could occur simultaneously. Firstly, the surfactant might act as a collector—adsorbing to the colloid surface by electrostatic attraction to anionic groups, increasing its hydrophobicity and affinity for the air bubble surface. Secondly, surfactant cations might adsorb at the air-water interface rendering air bubbles positively charged leading to increased attachment of the negatively charged wood extractive colloids and improved flotation. Figure 3-8, trace d) shows air bubbles are more positively charged in 100 mg/L DTAC. This provides evidence that the cationic surfactants adsorb to air bubbles. The flotation results in Figure 3-6 also support this. If the first mechanism dominated, flotation should improve with increased pH as the proportion of anionic groups at the colloid surface increases. This was

not the case. Rather flotation was improved at pH 3 and 5 but not at the higher pH 7. This is consistent with the zeta potential measurements in Figure 3-8 which show that air bubbles in 100 mg/L DCAC have a positive charge below pH 7 which would increase attachment of colloids. Adsorption of surfactant on the surface of air bubbles would also lead to an attractive van der Waals interaction. Thus, with both the electrostatic and van der Waals interaction being attractive, there should be no energy barrier to attachment and three-phase contact should result. The reduction in flotation efficiency with cationic surfactants at pH 7 (compared to that without added surfactant) might be explained as a reduction in surfactant flotation of resin and fatty acids resulting from competition for area on the air bubble surface. Adsorption of cationic surfactants on the air bubbles would reduce the area available for adsorption of extractives. The effect of pH will be further examined in Chapter 4.2.3.

Of the cationic surfactants, DTAB gave the best removal efficiency and was chosen for further flotation studies. The difference in effectiveness between the cationic surfactants may be due to their carbon chain length. The carbon chain is the hydrophobic part of the surfactant molecule. DTAB has a chain of twelve carbon atoms (C12), Quatramine 50 has a mixture of chain lengths between twelve and sixteen (C12-C16), and both CTAB and Quatramine 16/50 have sixteen (C16). At pH 5 the greatest flotation efficiency was achieved with the C12 surfactant followed by C12-16 then the C16 surfactants. Thus, over this small range, flotation efficiency decreased with increased chain length. Some valuable measurements were reported by Henderson et al. in a study on the effect of surfactant chain length on flotation of algae [110]. They measured two important properties of alkytrimethylammonium bromide surfactants of different chain lengths. These results are displayed in Table 3-6. The surface excess is the maximum surface concentration of surfactant at the air-water interface, which was shown to decrease with increased chain length due to accommodation of the longer chain at the surface [110]. This infers a higher possible surface charge density for a surfactant of shorter chain length. Another parameter (pC_{20}) was reported which was defined as the negative log of concentration of surfactant required to reduce the surface tension by 20 mNm^{-1}. This was found to increase with chain length indicating increased affinity for adsorption at the air-water interface.

Table 3-6 Properties of alkytrimethylammonium bromide surfactants. Data from Henderson et al. [110].

surfactant	chain length	surface excess Γ_m x 10^6 (mol m^{-2})	pC_{20}
DTAB (dodecyltrimethylammonium bromide)	12	2.59	2.26
MTAB (myristyltrimethylammonium bromide)	14	2.40	3.00
CTAB (cetyltrimethylammonium bromide)	16	2.16	3.62
OTAB (octadecyltrimethylammonium bromide)	18	1.38	4.60

That study found that flotation of algae improved with longer chain lengths which is opposite to results of the current study in which the shorter chain length of DTAB gave better flotation of extractives than CTAB (Figure 3-6). However, on closer analysis, the overall principle of improved flotation with higher bubble surface charge density may be consistent. After calculating the bubble charge at optimal flotation for each surfactant, Henderson et al. found that flotation efficiency correlated with higher charge density at the bubble surface. As it happened, the surface charge density was limited in their experiments by competing interactions with algal cells at high surfactant concentrations, which was more pronounced for the shorter chain lengths, resulting in higher surface charge densities with the longer chain lengths. Effectively, in that study the surface charge was determined by the affinity for the bubble surface (indicated by pC_{20}) rather than the surface excess. In the current study however, it may be determined by the surface excess. With surfactant concentrations approximately fifty times higher (80 mg/L of DTAB is equivalent to 0.26 mM compared to less than 0.005 mM in the literature study) it seems reasonable to assume that higher surface charge density would result. If the surfactant concentration is high enough, the surface excess concentrations may be reached in which case, the shorter chain length DTAB would result in a higher surface charge density on bubble surfaces leading to stronger bubble-particle attachment and higher flotation efficiency.

3.3 Conclusions

A lab-scale flotation method was developed for removal of wood extractives from TMP process water. A Denver D12 laboratory flotation cell was adapted by addition of a rotameter to measure airflow and water bath for temperature control as well as a custom built five litre cylindrical stainless steel flotation vessel. The vessel shape was found to be important for retaining water and allowing collection of a more concentrated froth.

A method for quantifying the flotation efficiency for removal of extractives was chosen based on the reduction of extractives concentration as measured by GC. Water loss should also be considered.

TMP process water was found to contain extractives in colloidal, dissolved and fibre-bound phases with the proportions dependant on pH. Most of the extractives however, were present in the colloidal phase over the full pH range of 3-8 studied indicating that flotation of colloidal extractives would be central to a successful flotation removal process.

The importance of using fibre-free process water to study flotation of dissolved and colloidal extractives was identified after flotation was found to selectively remove longer fibres particularly with cationic surfactants. This flotation of fibres contributed to flotation efficiency by removing fibre-bound extractives but hindered interpretation of results with regard to flotation of dissolved and colloidal extractives. Thus, to eliminate this problem, a low-fibre process stream was chosen for collection of TMP process water for further flotation studies.

Flotation with different surfactants over three pH values (3, 5 and 7) showed trends dependent on surfactant type (cationic, anionic and non-ionic). The trends were discussed in terms of flotation of colloidal extractives governed by surface forces and surfactant flotation of dissolved extractives by adsorption on bubble surfaces.

Cationic surfactants were found to be effective in aiding extractives flotation. This was attributed to the adsorption of the surfactant to air bubble surfaces creating a positive surface charge and increasing attachment of the negatively charged colloids. A surfactant carbon

chain length of 12 was more effective than 16 most likely because the higher maximum surface excess would result in a higher charge density on the air bubble surface.

The flotation method developed was then used to study the effects of flotation process parameters and process water composition on flotation efficiency as presented in Chapters 4 and 5.

Chapter 4 Effect of flotation process parameters

4.1 Introduction

Flotation of wood extractives is a complex process with many variables. Some variables are simple to control such as impeller speed or temperature, and others are more difficult or impractical to control such as dissolved organic matter and ionic strength as they are properties of the process water itself. This chapter deals with those variables that can be easily controlled. The process was optimised and insights into the mechanisms of flotation were obtained by studying the effect of each individual parameter on the flotation efficiency. The parameters studied were: the added surfactant concentration, flotation time, air flow, impeller speed, temperature and pH.

Zasadowski et al. published similar work using a 20 L Voith flotation cell, DTAC surfactant, and process water from a thermomechanical pulp and paper mill in Sweden processing wood from Norway spruce (*Picea abies*)[99]. That research found improved removal of pitch with a higher concentration of surfactant, higher airflow, higher temperature and lower pH [99]. Those results can be compared with the current work although the flotation cell and wood species are different. Zasadowski et al. reports flotation results as residual extractives which is the percentage of extractives remaining in the treated water rather that the percentage reduction reported in the current work.

Of the parameters to be investigated, related research in the literature provides insightful information for interpretation of flotation results.

Cationic surfactants are used as collectors or surface modifiers in the flotation of minerals such as quartz, as they can adsorb to the particle surface changing its surface properties. Increased concentration of dodecylamine collector has been shown to improve the flotation of quartz, up to a certain concentration at which bubble clustering occurred [118]. Surfactants also adsorb to bubble surfaces changing their charge [113].

Temperature affects the protonation, solubility and phase distribution of wood extractives [13, 69]. Higher temperature has been shown to lower the colloidal pK_a of resin and fatty acids thus increasing solubility and movement into the dissolved phase [13]. Generally, lower temperatures are associated with reduced colloidal stability and increased pitch deposition [45, 57]. For example, a study using laboratory prepared *P. radiata* pitch emulsions, found temperatures below 35 ºC resulted in increased deposition of pitch [45].

4.1.1 Bubble generation method

Bubble size is an important variable in flotation processes which has been shown to affect flotation efficiency. Bubble size is well known to be dependent on both mechanical properties of a flotation cell and the chemical properties of the solution [119]. In the current study bubble size was not measured but can be estimated and its effect on flotation inferred based on the main parameters that are known to determine bubble size: the bubble generation method [83, 108, 120], impeller speed [108], airflow [108], surfactant or frother concentration [120, 121], temperature [121, 122], pH [121] and ionic strength [121].

The bubble generation method is an important determinant of the bubble size. DAF generates very fine bubbles around 10-100 µm in diameter, whereas froth flotation or IAF generates bubbles around 350-3000 µm [83, 120]. Girgin el al. investigated the size of bubbles generated in a self-aerated Denver flotation unit identical to the one used in the current research [108]. They reported bubble sizes between 460 and 4500 µm. They also found that the bubble size increased with higher impeller speeds due to increased airflow into the unit. The effect was much less pronounced with higher concentrations of the frother Dowfroth 250 (1-(1-methoxypropan-2-yloxy)propan-2-ol, a non-ionic surfactant), which reduced the bubble size by inhibiting coalescence [108]. These relationships between bubble size and impeller speed and frother concentration can be assumed to apply qualitatively to the current study because the flotation unit is the same. Although differences may result from the different surfactant used and slightly higher airflows due to a different flowmeter attachment, it might be estimated that the bubbles generated in the current study with addition of DTAB were around 500 µm based on the literature.

Bubble size is known to be decreased with increased surfactant concentration [120, 121]. A common belief is that this is due to the lowered surface tension but there is poor correlation between surface tension and bubble size. Rather, evidence suggests that coalescence of bubbles at low surfactant concentrations produces larger bubbles [120]. Rodrigues and Rubio showed that the mean bubble size reduced drastically with addition of Dowfroth 250 frother despite only small changes in surface tension [120]. The bubble size distribution also showed a larger range in bubble sizes at low concentrations indicating coalescence of smaller bubbles to produce larger ones.

Bubble size has been shown to reduce with increasing temperature, explained by the decreased surface tension and viscosity [121, 122]. Increased ionic strength also decreases bubble size whereas increased pH leads to larger bubbles [121].

Smaller bubble size has been shown to improve flotation in a number of studies [123-125]. Yoon and Luttrell calculated the theoretical probabilities of collision and adhesion for flotation with different bubble and particle sizes [123]. Their calculations were based on the well understood theory and mechanisms of mineral flotation. Smaller bubble sizes (< 350 μm) were shown to give better adhesion, and these conclusions were backed up by laboratory studies on flotation of coal particles [123]. Other researchers have also reported improved flotation of different materials with smaller bubble sizes. Ahmed and Jameson showed flotation of quartz, zircon and polystyrene latex (particle size <50 μm) was drastically improved by reduction of bubble size from 655 to 75 μm [125]. Coward et al. showed flotation of microalgae (cell size <30 μm) [126] with CTAB surfactant was more efficient with smaller bubble sizes (mean diameter of 622 μm compared with 859 μm and 1229 μm) [124].

Alternatively, Eskanlou et al. showed that larger bubble sizes gave higher particle loading due to greater buoyancy [118]. They studied the flotation of quartz (particle sizes 50-300 μm) by column flotation with a needle sparging system for bubble generation (bubble sizes 0.8 and 1.8 mm) and using a dodecylammonium chloride collector and polypropylene glycol frother. They concluded that the optimal bubble size related to the particle size.

In summary, it appears from the literature that smaller bubble sizes improve flotation, except for larger heavier particles where greater buoyancy is required. Wood extractive colloids are very small at around 0.1 -3 µm in diameter [4, 60, 71] and have a similar density to water. Therefore, their flotation should be improved by smaller bubble sizes.

4.2 Results and Discussion

4.2.1 Surfactant concentration

Flotation was performed using a range of DTAB concentrations, all below the critical micelle concentration of 14 mM (4.3 g/L) [110]. The flotation efficiency was determined for each class of extractives as well as for the total extractives. Flotation efficiency of all components improved with increasing DTAB concentration as shown in Figure 4-1. The improvement reached a plateau at around 80 mg/L, therefore, this was the concentration chosen for all subsequent experiments.

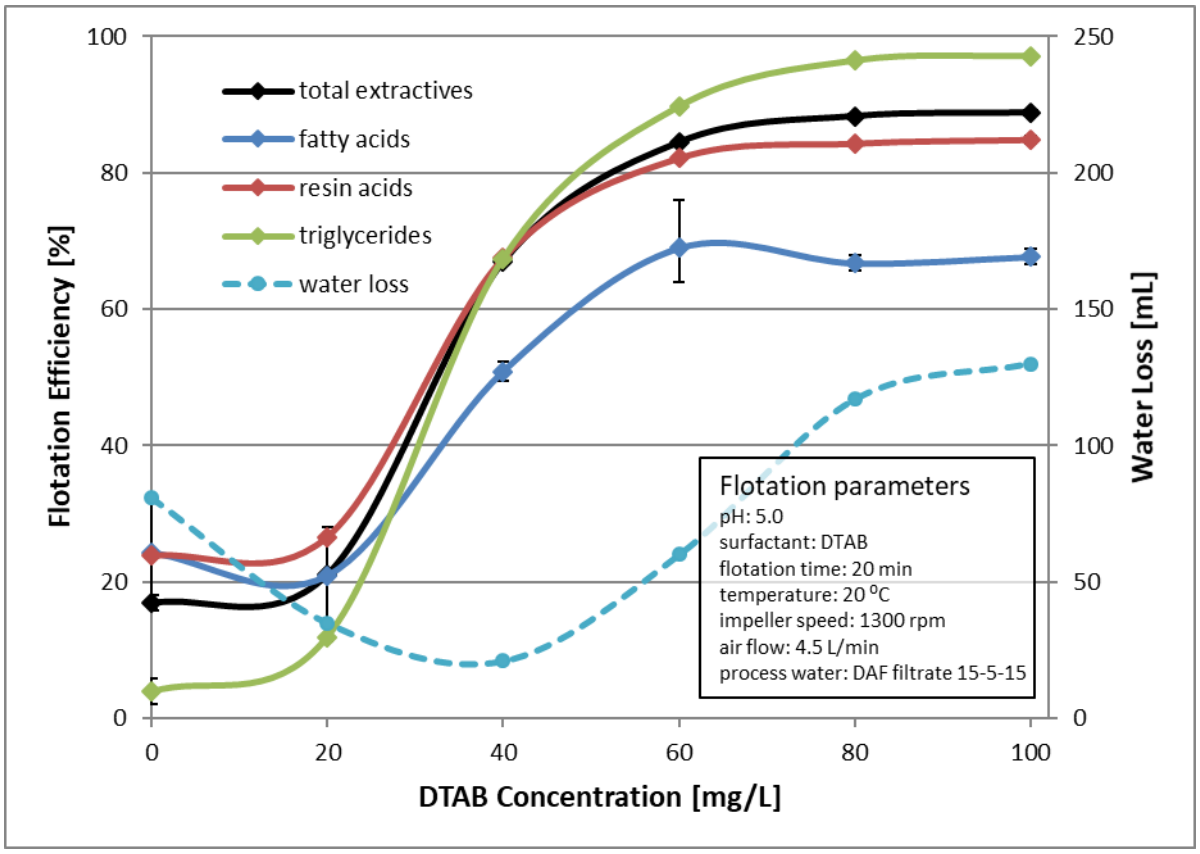


Figure 4-1 Effect of DTAB concentration on flotation of wood extractives

The improvement with increasing DTAB concentration can be explained by the increased electrostatic attraction between the cationic surfactant and resin and fatty acid anions. It may also be due in part to the reduction in bubble size that is known to occur with increased surfactant concentration [120, 121]. The plateau in flotation efficiency indicates some limiting factor. It may be that the maximum surface density of adsorbed DTAB on the bubble surface was reached above 80 mg/L and thus no increase in bubble charge occurred, therefore no increase in attachment of colloids was gained by higher concentrations. While flotation of triglycerides plateaued at close to 100%, the flotation of resin and fatty acids plateaued at lower levels. Flotation of triglycerides is taken to reflect colloidal flotation since triglycerides are almost exclusively in the colloidal phase whereas resin and fatty acids also exist in the dissolved phase (see Table 3-2). It may be that the DTAB concentration improves flotation of colloids more than flotation of dissolved extractives resulting in the observed lower flotation efficiencies for resin and fatty acids compared to triglycerides. Negatively charged wood extractive colloids will experience electrostatic attraction to air bubbles rendered positively charged by adsorption of DTAB, increasing colloidal flotation. Surfactant flotation of resin and fatty acids occurs when their anions adsorb to bubble surfaces. At pH 5, the concentration of resin and fatty acid anions is low (pK_a is around 7 for resin acids and around 7-10 for fatty acids [12]) but some interaction with DTAB may occur. This could result in ion pairs between resin or fatty acid anions and DTAB cations, insoluble complex formation or mixed micelles depending on the concentrations and ratio of surfactants [127, 128]. Ion pair formation in such a system is inhibited by electrolytes [129] because the single charge on an isolated ion is easily shielded. Conversely, mixed micelles or colloids with multiple charges will experience a greater electrostatic force and complexing ability with DTAB on bubble surfaces.

Zasadowski et al. found a similar trend of increased removal of wood extractives with added cationic surfactant DTAC over the range 40 to 80 ppm [99]. That work reported results for several temperatures and pH levels including 20 ºC and pH 5.1 which is very similar to the current study. Under those conditions residual pitch in the treated water dropped from 64 ± 2% with 40 ppm DTAC to 37± 1% with 80 ppm. This translates to 36 ± 2% and 63 ± 1% flotation efficiency which is below the values obtained in the current study but reflects the same trend. The difference may be due to the much higher proportion of resin acids in *P.*

radiata wood extractives of the current work compared with *P. abies* or to differences in bubble size, and cell dynamics.

4.2.2 Flotation time, airflow and impeller speed

Flotation time, airflow and impeller speed were initially studied separately but were found to be inter-related, so a combined study was undertaken. Air is drawn into the flotation vessel by the action of the impeller; thus airflow was dependent on the impeller speed as shown in Chapter 3.2.3. Figure 4-2 shows the effect of impeller speed on flotation. Flotation efficiency improved with increased impeller speed (and the resulting airflow) but with less effect at higher speeds. The water loss was minimal at the lower impeller speeds of 700 and 1000 rpm but increased dramatically with higher impeller speeds of 1300 and 1600 rpm. This appeared to be simply because the higher airflow at higher impeller speeds producing a greater volume of froth which inherently contained more water in the liquid film of bubbles. At the 1300 rpm recommended by the manufacturer, flotation efficiency was high and water loss was below 100 mL.

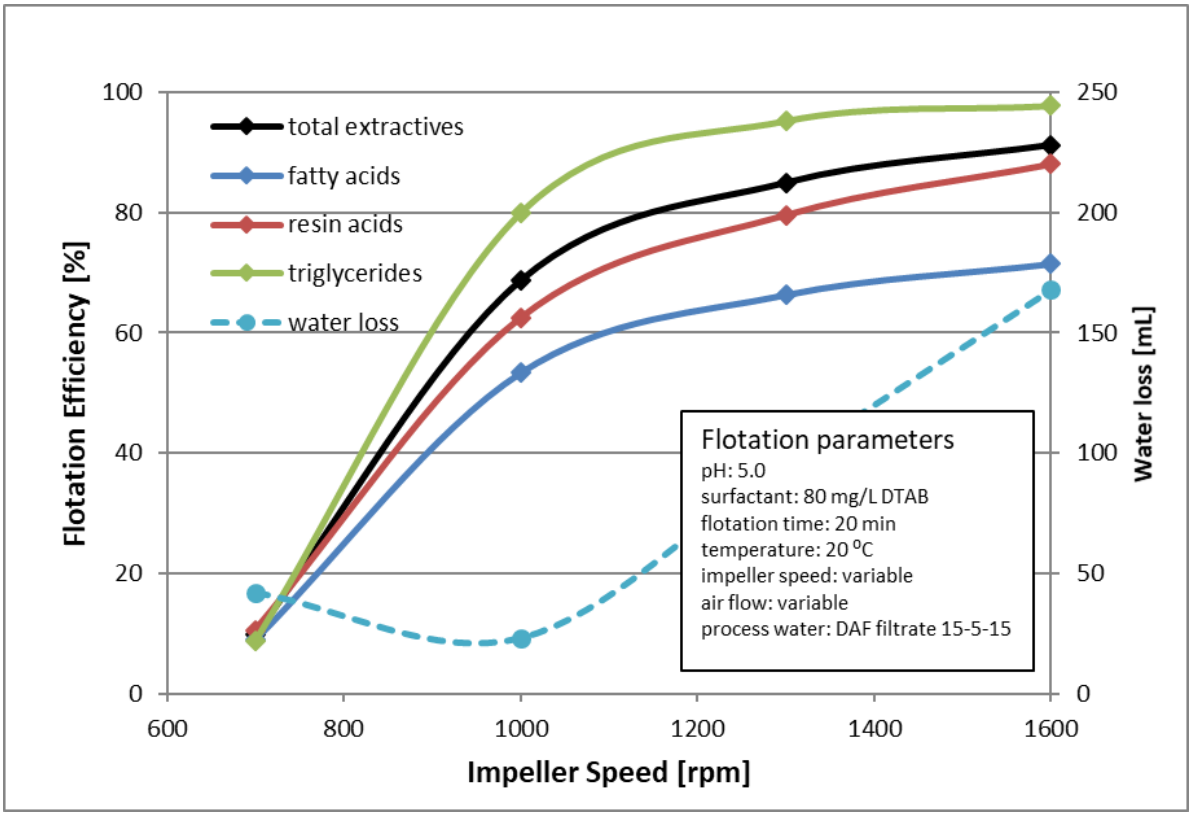


Figure 4-2 Effect of impeller speed on flotation of wood extractives

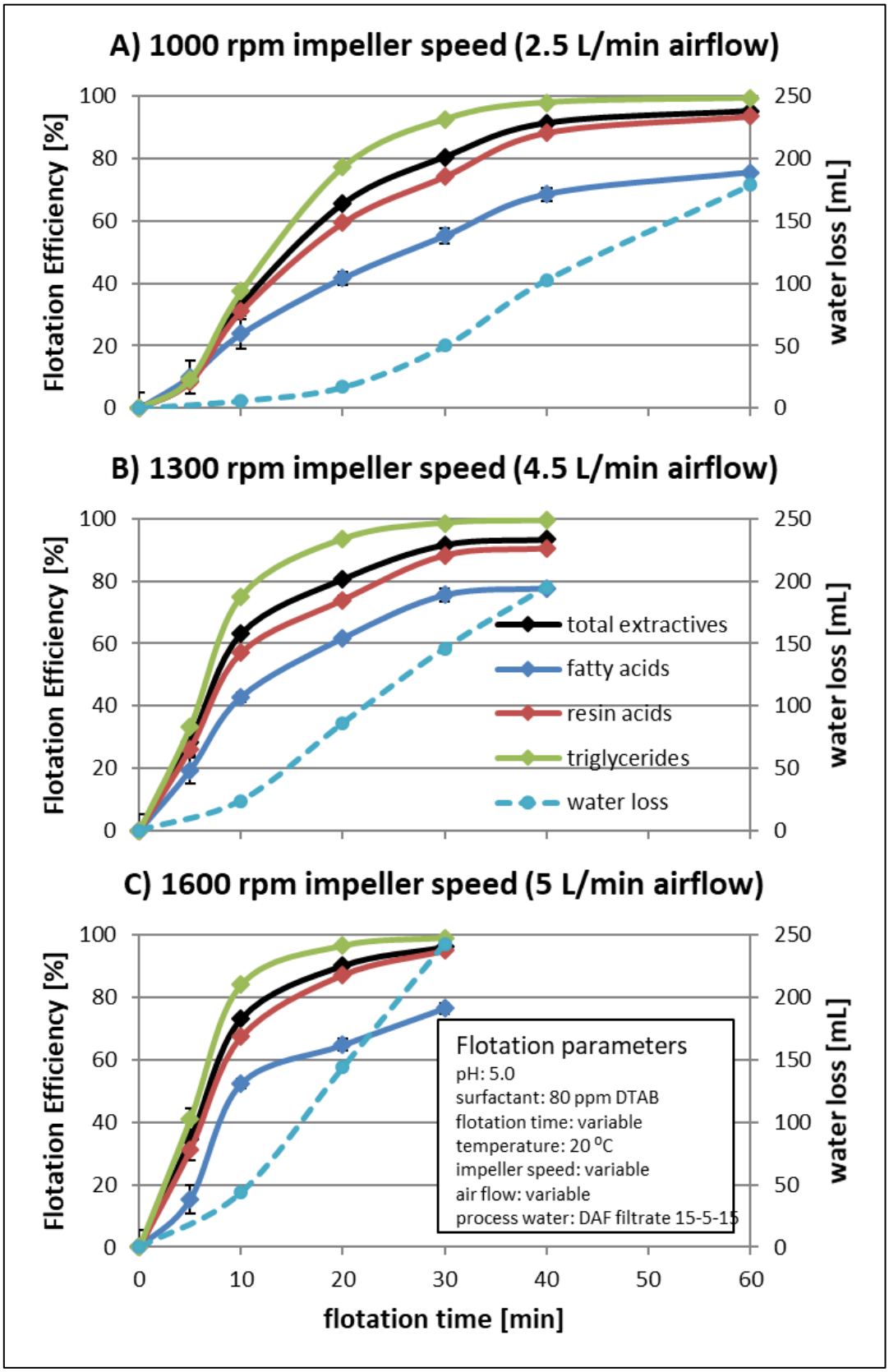


Figure 4-3 Effect of impeller speed, airflow and time on flotation of wood extractives

Figure 4-3 shows the relationship between flotation time and impeller speed/airflow. The flotation efficiency was plotted over time at three different impeller speeds (and airflows). At each impeller speed, a maximum removal efficiency of around 95% for total extractives was achieved but over different time periods. At the lower 1000 rpm, it required 60 min to reach this value whereas at 1300 rpm it took 40 min and at 1600 rpm only 30 min. The water loss however, increased at the higher impeller speeds. Optimal parameters therefore, depend on the hierarchy of priorities for removal efficiency, process speed and recovery of treated water. For experimental purposes, an impeller speed of 1300 rpm was chosen because this was the value recommended in the flotation machine instrument manual for a 1 L flotation volume. An optimal flotation time of 20 min was chosen as, at this time, the removal efficiency began to plateau while the water loss remained below 100 mL, which is less than 10% of the initial volume. In a continuous process, as would be employed in a pulp and paper mill setting, a similar balance could be achieved by altering process flow rates.

The trend for increased flotation efficiency with higher airflow appears to be simply due to an increased bubble surface area available for collection of extractives, which explains why the maximum flotation efficiency is still reached with lower airflow but requires longer flotation time. The change in bubble size with impeller speed should be minimal because the optimal concentration of DTAB should inhibit bubble coalescence as was observed in the work by Girgin et al. [108].

Zasadowski et al also studied the effect of airflow on a similar flotation system comparing results with no airflow to those with an airflow rate of 9 L/min [99]. An improvement in flotation was reported with the added airflow (a drop from 35% to 20% residual pitch). This shows a similar trend to the current work.

4.2.3 pH

The pH of *P. radiata* TMP process water without additives is around pH 5 but due to recirculation of water from different mill processes, the pH of process waters in a TMP mill can vary from pH 4 to 8. pH was expected to be an important variable in flotation due to its

effect on protonation of wood extractives and on their distribution between dissolved, colloidal and fibre-bound phases. The changes in flotation efficiency with pH were measured and are shown in Figure 4-4. Between pH 3 and 5, the flotation efficiency of all extractives classes was high. Below this range, at pH 2, there was a slight drop. Above this range, the flotation efficiency of triglycerides and fatty acids decreased while that of resin acids remained roughly constant. Water loss peaked at pH 4. The optimal pH chosen for subsequent experiments was pH 5 which is within the range for maximum flotation efficiency but outside that for maximum water loss and is also closest to the original pH of the process water, so required the least adjustment.

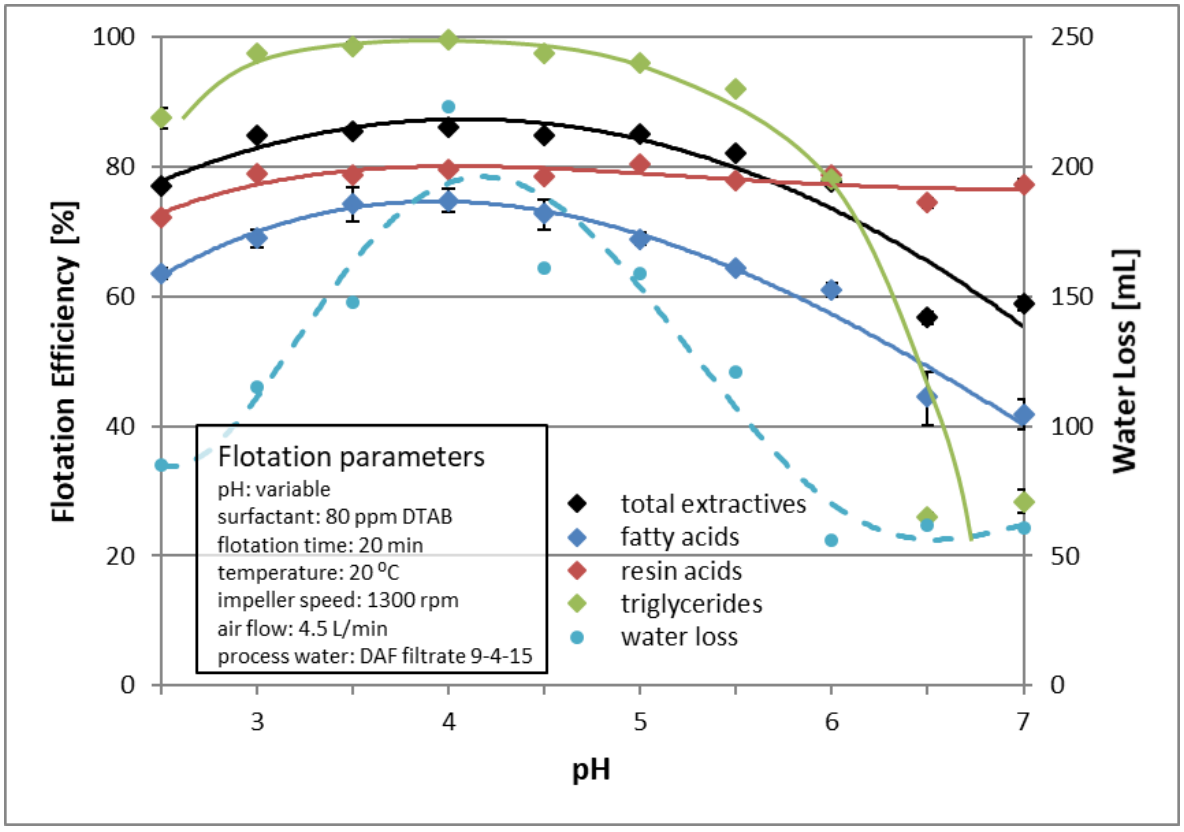


Figure 4-4 Effect of pH on flotation of wood extractives

Three flotation mechanisms are proposed to explain these trends in removal efficiency with pH: colloidal flotation, surfactant flotation and flotation of surfactant-extractive complexes. The observed flotation efficiency is a result of all these processes combined.

Colloidal flotation based on surface forces was predicted theoretically by Derjaguin in 1982 and called ‘contactless flotation’ [87] which can also be understood as flotation by attachment at a primary or secondary minimum in the interaction energy between particle and air bubble without rupture of the intervening film. It has since been identified as the mechanism for removal of wood extractives from TMP by Korpela [85]. In that study no surfactant was added, and the pH was not changed from its original value (pH 5). Under those conditions, electrostatic forces between air bubbles and colloids were repulsive (rather than attractive as in the current work) but flotation did occur. The author attributed this in part to the reduction of zeta potentials in the presence of calcium ions. This would reduce the electrostatic repulsion and may lead to a deeper secondary minimum in the interaction energy provided there is an attractive van der Waals component. The interaction energy between bubble and colloid includes the van der Waals component and electrostatic component. For the flotation results presented in Figure 4-4, the van der Waals component should be attractive due to adsorption of surfactant at the bubble surface [116, 117]. The electrostatic component should also be attractive due to the positive surface charge of bubbles and negative charge of colloids (as predicted by Figure 3-8). The sum of these interactions should lead to attachment of colloids to bubbles by either three-phase-contact or coagulation at a minimum in the interaction energy depending on the hydrophobicity of the colloid surface. The interaction is dependent on pH however, particularly due to the changes in the bubble surface charge with pH. Although air bubbles are predicted to be positively charged over most of the pH range studied, they will approach neutral around pH 7 (Figure 3-8). Additionally, increased adsorption of dissolved extractives around and above their pK_a values (around 7 for resin acids and around 7-10 for fatty acids [12]) may further reduce the bubble charge. These proposed trends are reflected in the results in Figure 4-4, most clearly in the flotation results for triglycerides. Triglycerides exist predominantly in the colloidal phase across the full pH range studied, therefore triglyceride flotation reflects the colloidal flotation. Triglyceride flotation efficiency was over 90% between pH 3 and pH 5.5 and above this range it plummeted to below 30% by pH 7. This coincides with the data already presented in Figure 3-8 showing changes in zeta potentials of colloids and air bubbles with pH. In the presence of the cationic surfactant DTAC air bubbles are shown to have a positive charge at lower pH reducing to zero around pH 7 and becoming increasingly negative above pH 7.

Colloids displayed a negative surface charge which decreased in magnitude at lower pH, approaching zero around pH 2.5. Maximum attraction between the two would be expected when there is a large positive charge on the bubbles and large negative charge on the colloids which is around pH 3 to pH 6 coinciding with the peak flotation efficiency for triglycerides. Flotation would also be expected to reduce dramatically (as observed) when air bubbles become negatively charged because the electrostatic repulsion would hinder attachment of colloids. Colloidal flotation is concluded to be highly dependent on electrostatic attraction between colloids and air bubbles thus is dependent on pH which affects the surface charges.

The wood extractive colloids contain resin and fatty acids as well as triglycerides which would also be removed by colloidal flotation. However, flotation efficiency for resin and fatty acids did not drop drastically above pH 6 as it did for triglycerides, which suggests another mechanism for flotation of these classes at the higher end of the pH range. Suggested mechanisms are surfactant flotation and flotation of extractive-surfactant complexes.

Surfactant flotation is an established mechanism utilised for the removal of surfactants from wastewater and may be called foam fractionation [84]. It has also been described for removal of resin and fatty acids from caustic Kraft mill effluent [90]. Resin and fatty acids anions act as anionic surfactants and can adsorb at bubble surfaces to be removed by flotation. Surfactant flotation would be expected to increase with pH as resin and fatty acids are deprotonated, becoming more surface active and moving from the colloidal to the dissolved phase where they can readily adsorb to bubble surfaces. The maximum flotation efficiency for total extractives was observed at pH 3-5 which is below the pK_a values for extractives (around 7 for resin acids and around 7-10 for fatty acids [12]). This maximum is not likely to be due to surfactant flotation which should occur at the higher end of the pH scale. Surfactant flotation may however explain the high flotation efficiency for resin acids at pH 5-7 especially in comparison to triglycerides which are not surface active and cannot be floated as surfactants. Fatty acids also displayed higher removal efficiency in comparison to triglycerides at higher pH which can be explained by surfactant flotation.

A third possible mechanism for flotation of extractives is flotation of complexes formed between resin and fatty acids and DTAB. Bonding between the organic acids is expected to

be strongest around their pK_a because the 50:50 mixture of carboxylate anions and carboxyl groups gives the greatest potential for ion-dipole bonding [130]. Complex formation between anionic and cationic surfactants is known to result in precipitation dependant on concentrations of the anions and cations [127, 131]. Such complexes could precipitate in solution or on bubble surfaces where dissolved extractive anions can come into contact with DTAB cations. The resulting complexes would be neutral and hence unlikely to be attracted to the positively charged air bubbles. Consequently, it seems unlikely that complexes formed in solution would be floated. A more likely scenario is flotation of complexes formed with DTAB already on the bubble surface which would result in attachment of the extractives to air bubbles.

The observed changes in flotation efficiency with pH (Figure 4-4) could result from the three proposed flotation mechanisms. The triglyceride flotation efficiency represents only colloid flotation since triglycerides are not surface active and can't be floated by the surfactant flotation mechanism and don't form anions so are unlikely to form complexes with DTAB. Resin and fatty acids which could be floated by all three mechanisms show a broader range of high flotation efficiency. The efficiency remains high above pH 5 due to increased surfactant flotation and flotation of extractive-surfactant complexes despite reduced colloid flotation.

Visual evidence for the proposed mechanisms is provided in Figure 4-5 which shows the change in appearance of process water before and after flotation treatment at pH 4.0 compared to pH 7.0.

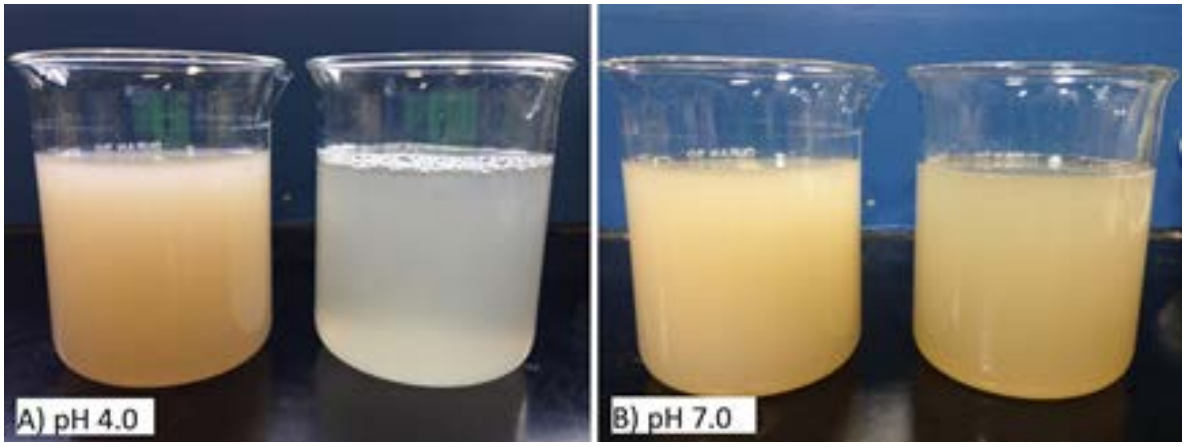


Figure 4-5 Change in appearance of process water before and after flotation treatment

There is a clear reduction in turbidity and colour at pH 4.0, indicating removal of colloids. The measured flotation efficiency was 86% for total extractives, 75% for fatty acids, 80% for resin acids and 100% for triglycerides. By comparison, at pH 7.0, little visible difference is observed despite the reduction in extractives concentration, indicating removal of dissolved extractives rather than colloids. The measured flotation efficiency at pH 7 was 59% for total extractives, 42% for fatty acids, 77% for resin acids and 28% for triglycerides.

A further study was undertaken to determine the effect of pH on flotation without the added surfactant with results presented in Figure 4-6. While the removal efficiencies are low, the results serve to support the proposed flotation mechanisms.

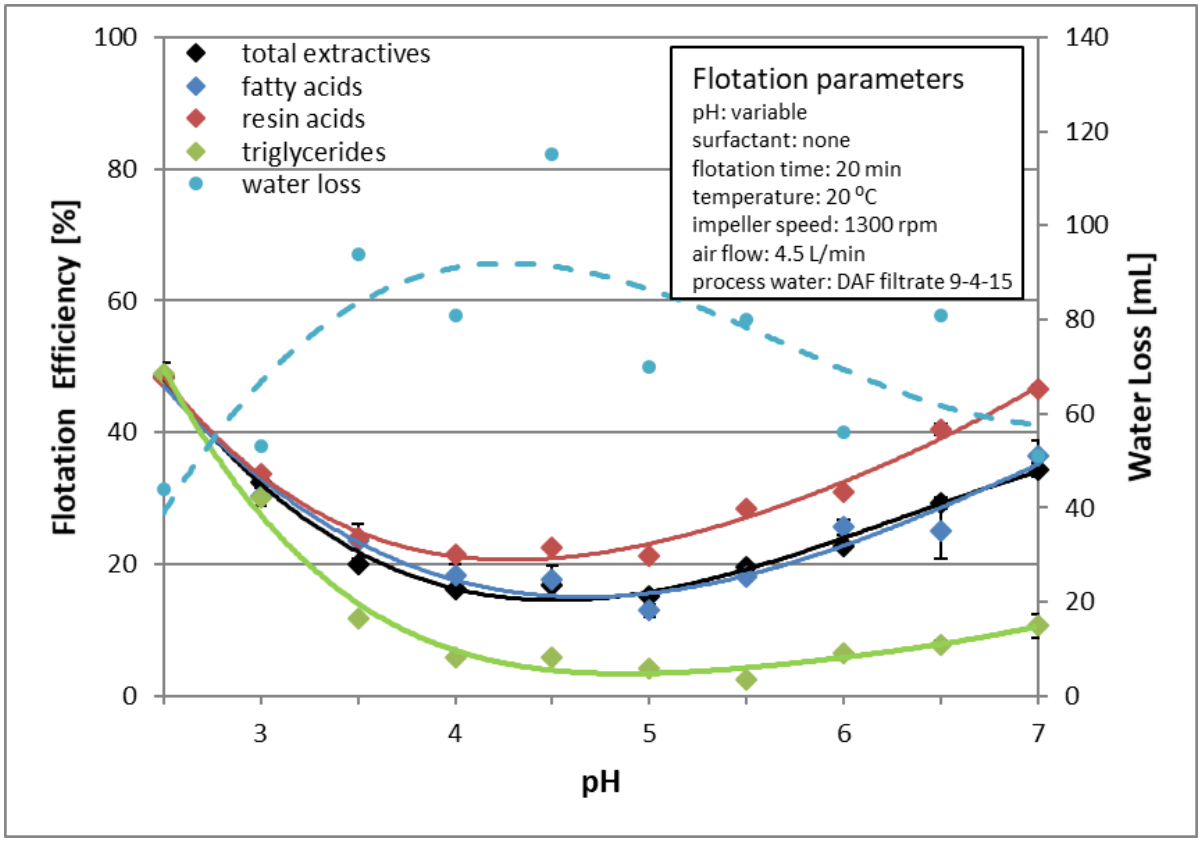


Figure 4-6 Effect of pH on flotation of wood extractives with no added surfactant

The van der Waals interaction between colloids and air bubbles in water is expected to be repulsive in the absence of surfactant as indicated by a negative effective Hamaker constant

(see Equation 9 where $A_{air} < A_{water} < A_{extractives}$ [74, 75]). This may reverse at pH levels above the pK_a as dissolved resin and fatty acid anions could then adsorb on the bubble surfaces. Without the cationic surfactant, air bubbles are expected to be slightly positively charged below pH 4.5 and slightly negatively charged at higher pH (Figure 3-8). Therefore, electrostatic attraction between colloids and air bubbles can only occur below pH 4.5. The flotation results do indeed show minimal removal of extractives at pH 4.5, near the expected zero charge on air bubbles, and improvement in removal of all extractive classes below this, indicating colloidal flotation. Above pH 4.5 removal efficiency of resin and fatty acids increased, while removal efficiency of triglycerides did not increase substantially, indicating mainly surfactant flotation of only the resin and fatty acids. Films of fatty acid salts have been found to be most stable at their pK_a due to ion-dipole bonding between carboxylate and carboxyl groups [130]. This may then contribute to the increased flotation efficiency at pH 7. The slight increase in triglyceride flotation may be due to increased colloidal flotation due to adsorption of resin and fatty acids on the bubble changing the effective Hamaker constant and hence the van der Waals interaction.

The effect of pH on bubble size may contribute to the observed flotation efficiencies, since pH has been reported to influence bubble size (with higher pH producing larger bubbles) [121]. This should result in better flotation efficiency at low pH and may have contributed to the broad maximum efficiencies in flotation with DTAB (Figure 4-4) and the improved flotation at lower pH without added surfactant (Figure 4-6).

The results of this study of the effect of pH are consistent with those of Zasadowski and Strand et al who looked at the effect of pH on flotation of wood extractives with a cationic surfactant [99, 101]. They reported the highest removal of extractives at around pH 3 (compared with pH 5 or 8). Their results also showed higher removal of resin and fatty acids compared to neutral extractives at pH 7.6 [99] indicative of surfactant flotation at higher pH.

A recent study by Xia et al. reported enhancement of flotation of coal particles with positively charged microbubbles [132]. In the study extended DLVO theory was used to model the interaction energies between particles in agreement with their experimental results. The study is of interest in comparison with the current work because some basic parameters

are similar. The coal particles were negatively charged and displayed some surface hydrophilicity due to impurities [132] making them similar to wood extractive colloids. The microbubbles were positively charged by addition of CTAB [132] similar to the DTAB used in the current study. The modelled interaction energy between coal particles and air bubbles without CTAB showed a primary and secondary minimum separated by an energy barrier, whereas the modelled interaction energy between coal particles and charged microbubbles was one of attraction increasing exponentially with proximity [132]. Similar interaction energies might be expected between wood extractive colloids and air bubbles with and without DTAB. The presence of a primary and secondary minima in the interaction energy between the particle and air bubble show that attachment may be possible under some conditions without added surfactant, while the attractive interaction between the particle and positively charged bubble show an overall attraction as was observed in the current study with addition of DTAB.

4.2.4 Temperature

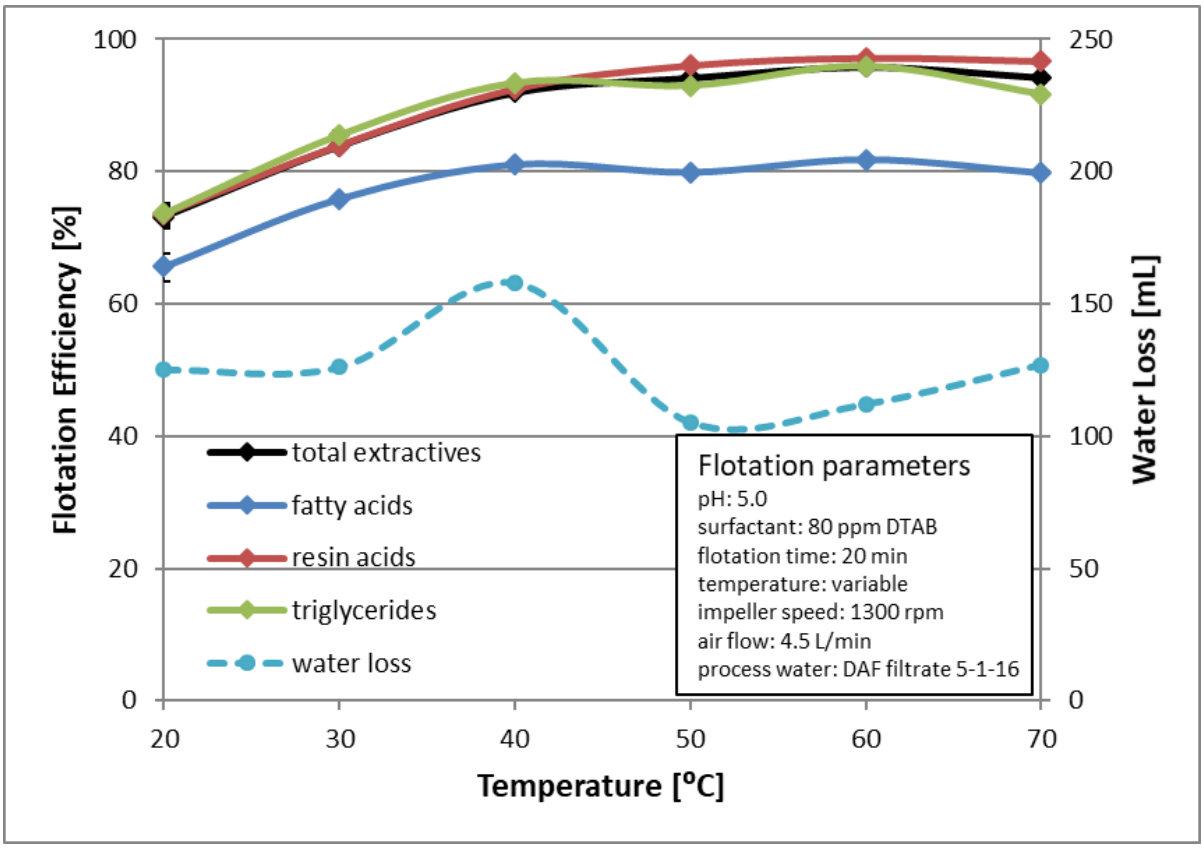


Figure 4-7 Effect of temperature on flotation of wood extractives

The influence of temperature on flotation was studied over the range of 20 to 80 ºC and the results are presented in Figure 4-7. An increase in removal efficiency with temperature up to 60 ºC was observed after which there was no further increase. Therefore, 60 ºC was chosen for optimal flotation which is conveniently within mill operating conditions of around 50 to 70 ºC. The increases in flotation efficiency with temperature applied to all extractive classes so is most likely due to an influence on colloidal flotation. There are several possible explanations for this. Bubble size is known to reduce with temperature due to reduced water viscosity and surface tension [121, 122] to improve flotation. There is also a change in resin acid pK_a values with temperature from around 7 at 20 ºC to around 6 at 50 ºC [13]. This would imply a slightly higher degree of deprotonation at higher temperatures. Assuming the resin acids remain in colloidal phase, this would increase the negative surface charge on the colloids leading to increased attachment to positively charged air bubbles and improve the flotation efficiency. Increased Brownian motion at higher temperatures may also increase the probability of attachment of colloids to air bubbles. The effect of temperature on the zeta potential of air bubbles is another possible explanation, as increased temperature has been observed to reduce zeta potential magnitude (whether positive or negative) [113]. This is reportedly due to either reduced surfactant adsorption or false zeta potential readings caused by increased Brownian motion affecting the measurement of electrophoretic mobility [113]. The reported reduction in zeta potential (with 100 mg/L DTAC) was greatest between 10 and 25 °C and very slight from 25 to 70 °C [113] which is consistent with the current observation of improvement in flotation efficiency with temperature.

Zasadowski et al. [102] and Strand et al.[99] also achieved optimal flotation of wood extractives at the higher temperature of 50 ºC compared to 20 ºC.

4.2.5 Reproducibility of the optimal method

To obtain a measure of reproducibility, the flotation method was performed five times using optimal process parameters with two different batches of process water. The results are presented in Table 4-1 and characterisation of the two batches of process water in Table 4-2.

Table 4-1 Reproducibility of flotation method

	1	**2**	**3**	**4**	**5**	**mean**	**sd**
flotation efficiency [%] (DAF filtrate 05/01/2016)							
total extractives	95.9	94.9	94.3	94.9	93.9	**95**	**0.7**
fatty acids	81.8	78.3	80.3	78.4	77.7	**79**	**2**
resin acids	97.2	97.4	97.1	97.1	96.7	**97**	**0.2**
triglycerides	95.9	92.8	91.3	93.1	90.8	**93**	**2**
water loss	112	103	81	91	100	**97**	**12**
flotation efficiency [%] (DAF filtrate 23/01/2018)							
total extractives	94.6	95.3	95.2	95.2	94.5	**95**	**0.4**
fatty acids	67.3	68.1	67.6	67.3	42.9	**63**	**11**
resin acids	97.6	97.5	97.5	97.4	97.6	**98**	**0.05**
triglycerides	92.6	94.6	94.4	94.5	95.2	**94**	**1.0**
water loss	71	98	123	108	99	**100**	**19**

The low standard deviations show very good reproducibility of the method. The similarity of results between the two batches also show good repeatability with different batches of water.

Table 4-2 Characterisation of process water used for reproducibility

batch	**1**	**2**
source	DAF filtrate	DAF filtrate
date	05/01/2016	23/01/2018
pH	6.0 ± 0.0	6.7 ± 0.0
Conductivity mS/cm	0.50 ± 0.01	0.51 ± 0.00
Calcium mg/L	13	18
Carbs g/L	1.70 ± 0.03	1.58 ± 0.04
Fibre %	0.069 ± 0.003	0.072 ± 0.004
Fibre	0.009 ± 0.001	0.031 ± 0.002
Total extractives mg/L	298 ± 1	285 ± 6
Fatty acids mg/L	18 ± 0	12 ± 0
Resin acids mg/L	202 ± 1	189 ± 4
Triglycerides mg/L	78 ± 1	84 ± 3

dissolved	12 %	17 %
Colloidal	74 %	69 %
Fibre bound	13 %	14 %

4.3 Conclusions

By studying the effect of various flotation process parameters on flotation efficiency, the flotation method was optimised and several mechanisms for flotation of wood extractives were proposed. The optimised method proved to be reproducible.

Table 4-3 Summary of the effect of process variables on flotation

process parameter	optimum	effect on flotation efficiency
DTAB concentration	80 mg/L	increase
flotation time	20 min	increase
airflow	4.5 L/min (dependent on impeller speed)	increase
impeller speed	1300 rpm (recommended by manufacturer)	Increase (by increasing airflow)
pH	5	peak pH 3 – 5 (colloid flotation) increase (surfactant flotation)
temperature	60 °C	increase

The optimal parameters identified were 80 mg/L DTAB, 1300 rpm impeller speed, 4.5 L/min airflow, 20 min flotation time, 60 ºC and pH 5 as summarised in Table 4-3. The flotation efficiency obtained under these conditions was: a 96 ± 0% reduction in total extractives, 97 ± 0% in resin acids, 82 ± 0% in fatty acids and 96 ±0% in triglycerides with 11% water loss.

The flotation parameters (DTAB concentration, flotation time, airflow, impeller speed and temperature) were all found increase flotation efficiency with decreasing effect at higher values. The optimal values were selected at a point where the rate of improvement levelled out thus obtaining maximum gain in flotation efficiency for minimal input of additives, time or energy.

The effect of pH on flotation efficiency was more complex, as it differed between the extractive classes (resin acids, fatty acids and triglycerides). Those results combined with studies of surface charges and phase changes (both original and from the literature) were combined to form a model for wood extractives flotation based on flotation of both colloids and dissolved extractives.

Colloid flotation was maximised by electrostatic attraction between air bubbles and wood extractive colloids and was optimal between pH 3 and 5. Flotation of dissolved extractives increased with pH and resulted from adsorption of resin and fatty acid anions to air bubble surfaces by either adsorption as surfactants or by formation of complexes with DTAB on the bubble surface.

Chapter 5 Influence of process water composition on flotation

5.1 Introduction

TMP process water is a complex mixture containing many components that may affect the flotation efficiency. Characteristics of the process water also varied between batches even when collected from the same process feed. This was due to seasonal variation in wood composition and the different processes that operate in the mill depending on the type of paper in production. This chapter relates to those characteristics of the process water that cannot be easily changed but nonetheless influence flotation efficiency. Linear regression analysis was used to identify correlations between the routinely measured process water characteristics and flotation efficiency. Additionally, some characteristics (ionic strength, dissolved organic wood polymers, and residual flocculant) were also investigated directly. The optimised flotation method was then carried out on TMP water from Norske Skog's Albury mill which had different composition to the process water from Boyer mill used to develop the method.

5.2 Results and Discussion

5.2.1 Linear regression analysis

A total of 18 different batches of DAF filtrate process water (listed in Appendix B) were used to perform linear regression analyses to identify which characteristics of the process water correlated with flotation efficiency. Each batch of process water was characterised by measuring pH, conductivity, fibre content, calcium concentration and dissolved carbohydrates as well as extractives concentrations. Each batch was also subjected to a standard flotation procedure using the parameters: pH5, 80 mg/L DTAB, 20 min flotation time, 20°C, 1300 rpm impeller speed, 4.5 L/min airflow. The flotation efficiency was determined for each class of extractives (fatty acids, resin acids and triglycerides) as well as the combined total. There are several limitations which should be kept in mind when drawing

conclusions from analyses such as this which rely on chance variations in the industrial process. This is because the variations are not necessarily random but result from process changes and operator decisions. Firstly, the range covered by each variable may be narrow since the process is likely to be controlled within certain limits, hence any trend or relationship found may not apply to a wider range. Secondly, variables may be linked leading to correlations that are not causational. Therefore, the correlations identified by these regression analyses were further studied in controlled experiments.

The graphs in Figure 5-1 to Figure 5-6 show removal efficiency plotted against each measured process water characteristic and the linear model for removal efficiency of total extractives. The residual plots (included in Appendix D) showed random distribution of residuals around zero which indicates that a linear model is appropriate. Since this was an observational study, it was not possible to hold the other variables fixed when plotting the regression of each individual characteristic. Thus, high residuals and low R^2 values were expected. The figures are displayed in descending order of correlation with flotation efficiency as quantified by the R^2 value.

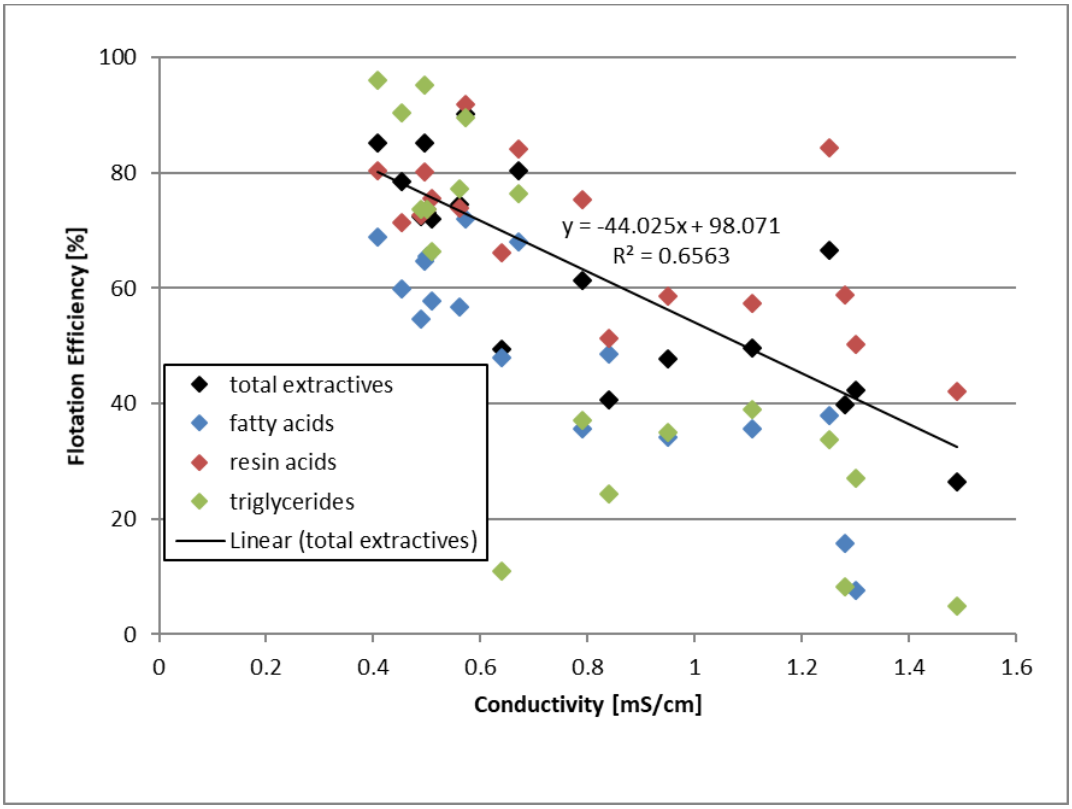


Figure 5-1 Correlation between conductivity and flotation efficiency

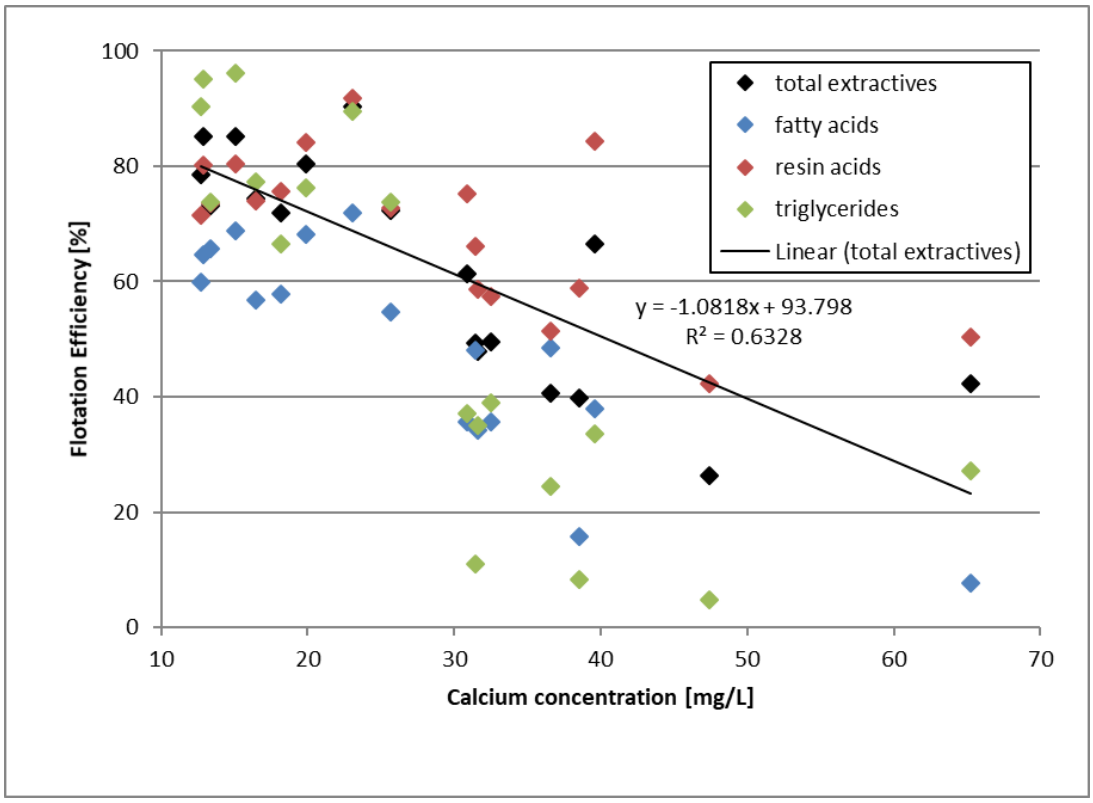


Figure 5-2 Correlation between calcium concentration and flotation efficiency

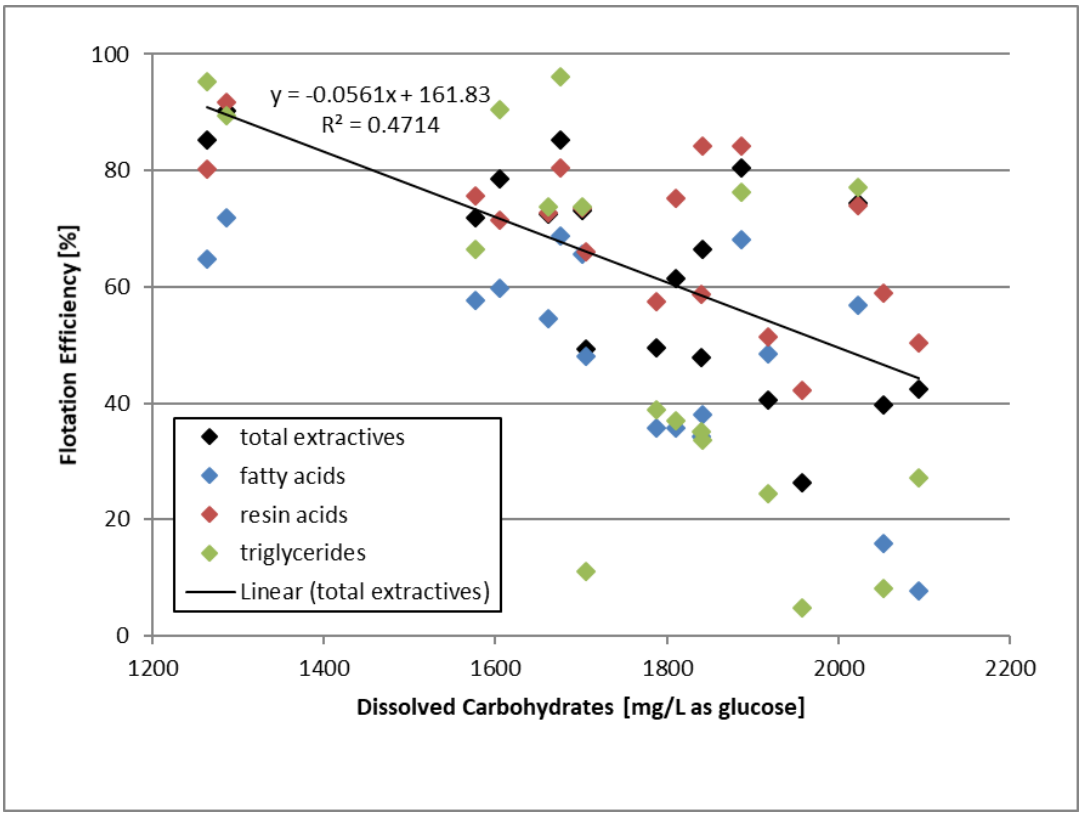


Figure 5-3 Correlation between dissolved carbohydrates and flotation efficiency

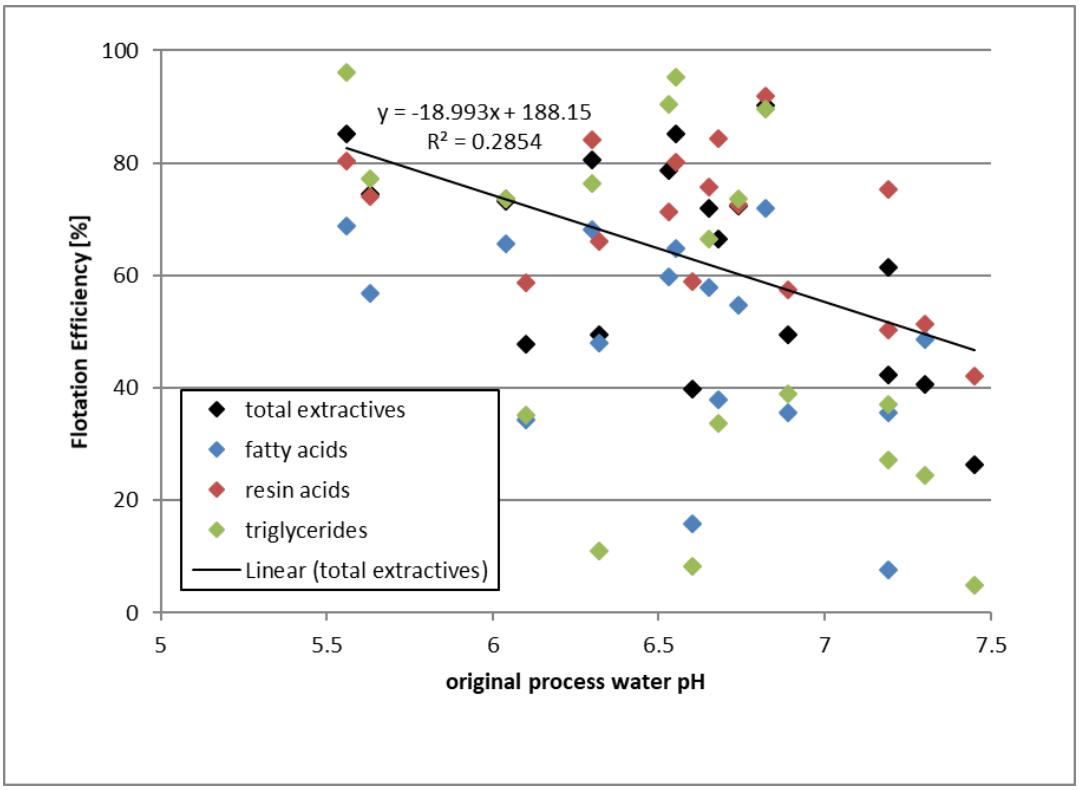


Figure 5-4 Correlation between original pH and flotation efficiency

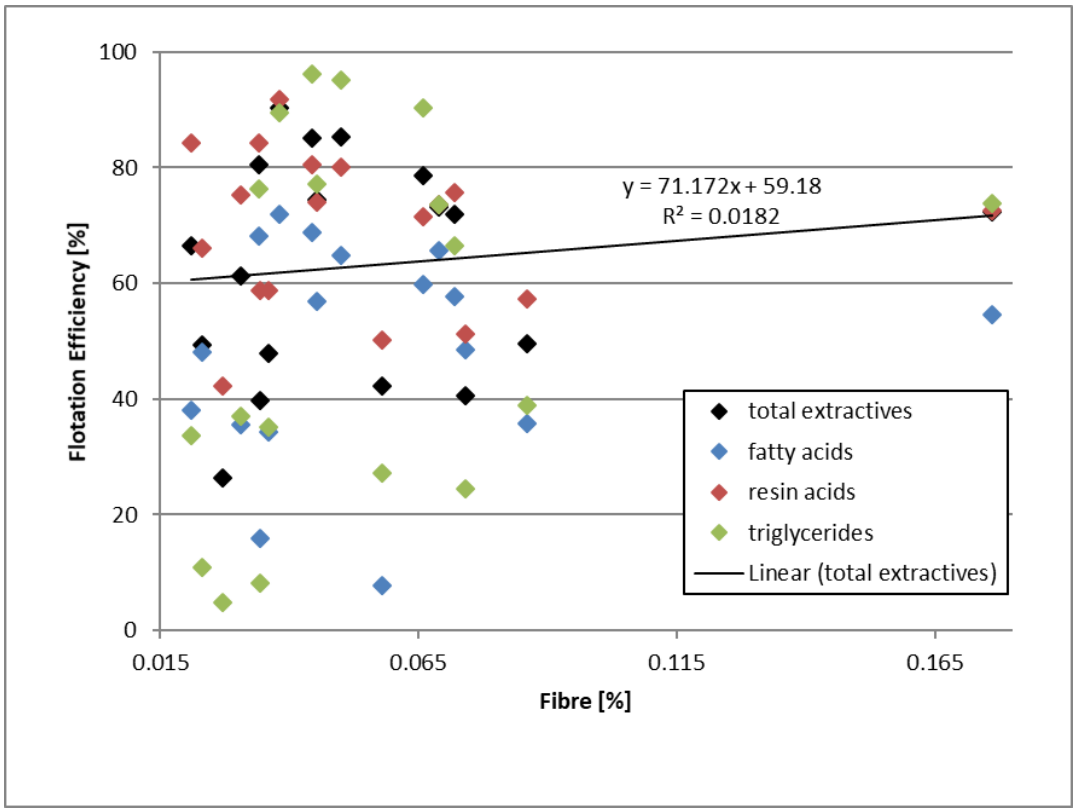


Figure 5-5 Correlation between fibre content and flotation efficiency

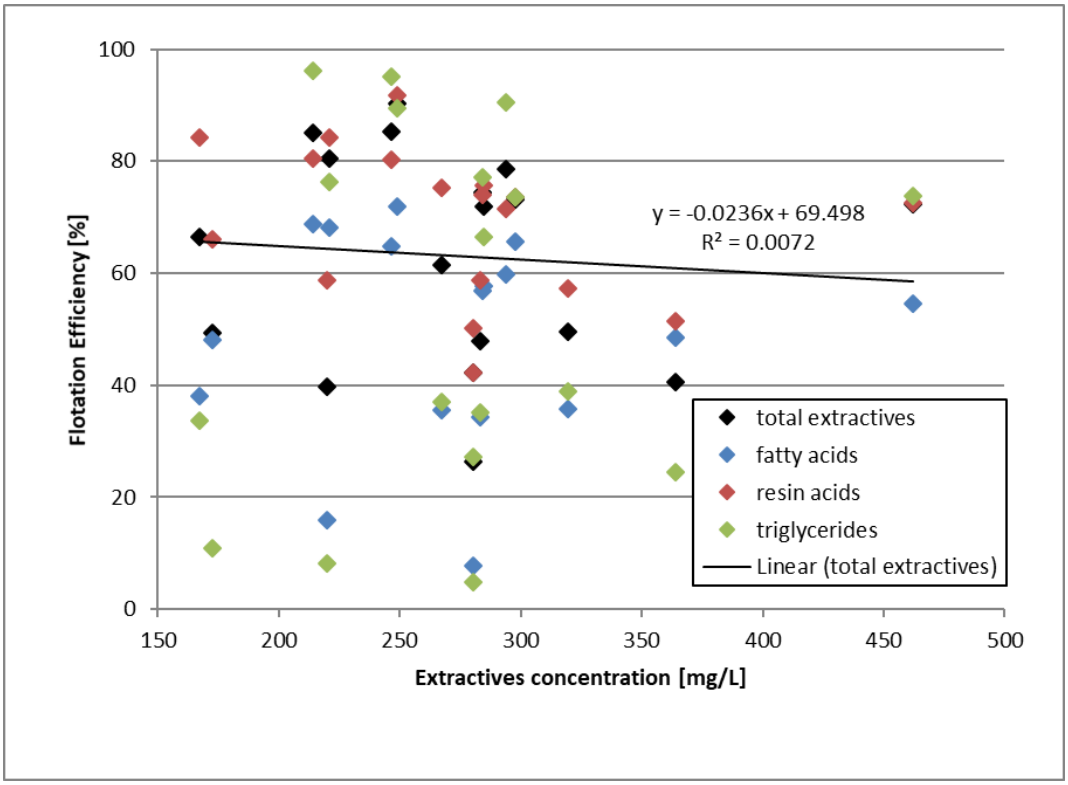


Figure 5-6 Correlation between extractives concentration and flotation efficiency

Conductivity in Figure 5-1 showed the strongest correlation (R^2 = 0.6563) followed by calcium concentration in Figure 5-2 (R^2 = 0.6328), dissolved carbohydrates in Figure 5-3 (R^2 = 0.4714), original process water pH in Figure 5-4 (R^2 = 0.2854), fibre in Figure 5-5 (R^2 = 0.0182), and lastly extractives concentration in Figure 5-6 (R^2 = 0.0072) which showed the weakest correlation.

Among the characteristics studied, conductivity and calcium concentration were identified as the strongest predictors of flotation efficiency, giving lower efficiency for higher conductivity and higher calcium concentration. Compression of the electrical double layer around both colloids and air bubbles which occurs with increasing conductivity and calcium concentration, is the likely reason for this indicating the importance of electrostatic forces to efficient flotation. Being a divalent cation, calcium has a stronger effect on this compression of the electrical double layer than monovalent ions such as sodium [75].

The influence of dissolved carbohydrates on flotation efficiency is less than that of conductivity or dissolved calcium, but with an R^2 value of 0.4714 is considered meaningful. Dissolved carbohydrates in solution contribute to stabilisation of the wood extractive colloids by steric effects which prevent the colloids from coming into close proximity with each other or with air bubbles [60, 74]. It may be that increased steric stabilisation also prevented short range interactions between colloids and air bubbles reducing flotation efficiency. This explains the negative correlation in Figure 5-3 which predicts lower flotation efficiency with increased dissolved carbohydrates.

The correlation between original process water pH and flotation efficiency is low, with an R^2 value of 0.2854. It should be noted that flotation was performed at a constant pH of 5.0 after adjustment of the original process water pH. The correlation with original pH may therefore be a secondary effect of the dependence on calcium concentration since the presence of calcium carbonate raises the pH.

The correlation of fibre content and extractives concentration with flotation efficiency was very low with R^2 values below 0.02 (Figure 5-5 and Figure 5-6). Thus, these variables were not considered to be predictors of flotation efficiency.

Table 5-1 Linear regression data for individual extractives classes

Process water characteristic	total extractives	resin acids	fatty acids	triglycerides
A. Conductivity				
R^2	0.66	0.43	0.84	0.67
gradient [pp.cm/ms]	-44	-26	-57	-75
B. Calcium concentration				
R^2	0.63	0.46	0.77	0.64
gradient [pp.L/mg]	-1.1	-0.66	-1.4	-1.8
C. Dissolved carbohydrates				
R^2	0.47	0.38	0.45	0.42
gradient [pp.L/mg]]	-0.056	-0.036	-0.062	-0.089

In addition to modelling the flotation efficiency for total extractives, linear regression models were fitted for each individual class of extractives (resin acids, fatty acids and triglycerides). The data plots are included in Figure 5-1 to Figure 5-6, but for simplicity, the linear models are not displayed on the graphs. Rather, the R^2 values and gradients for the most predictive characteristics are presented in Table 5-1. The R^2 value indicates the strength of the correlation, whereas the gradient indicates the magnitude of the effect of that variable on flotation efficiency.

For the three characteristics presented (conductivity, calcium concentration, and dissolved carbohydrates), the extractives class exhibiting the strongest correlation with flotation efficiency (highest R^2) was the fatty acids, followed by triglycerides then resin acids. This means that these characteristics are better predictors for the fatty acid and triglycerides flotation efficiency than for resin acids. However, even for the resin acids, they are considered to be meaningful predictors.

For each of the three characteristics presented, the extractives class showing the steepest gradient was the triglycerides followed by fatty acids then resin acids. This means that flotation of triglycerides was more affected by changes in conductivity, calcium concentration, and dissolved carbohydrates. This may be because triglycerides exist almost exclusively in the colloidal phase and colloid flotation is dependent on surface forces including electrostatic attraction which is affected strongly by these variables. On the other hand, resin and fatty acids exist in dissolved and fibre bound phases as well as the colloidal phase. Consequently, they can be floated by other mechanisms such as surfactant adsorption and entrainment of fibre particles. This explanation is supported by the previously presented phase distribution of extractives (Table 3-2) which showed 94% of triglycerides, but only 69% of fatty acids and 64% of resin acids were in the colloidal phase at pH 5. Thus, the higher the proportion in colloidal phase, the more flotation efficiency was affected by conductivity, calcium concentration, and dissolved carbohydrates.

5.2.2 Ionic strength

Ionic strength is a measure of the total electrolyte concentration of a solution and is also related to conductivity. In TMP process water, a major contributor to ionic strength and conductivity are the calcium and bicarbonate ions produced by dissolution of calcium carbonate, used as a filler in paper production [133]. Therefore, the effect of additional calcium carbonate on flotation was studied. The added calcium carbonate was assumed to fully dissolve in the process water at pH 5 which was evidenced by increases in conductivity. The effect of sodium chloride was also studied for comparison, and the results are presented in Figure 5-7 and Figure 5-8.

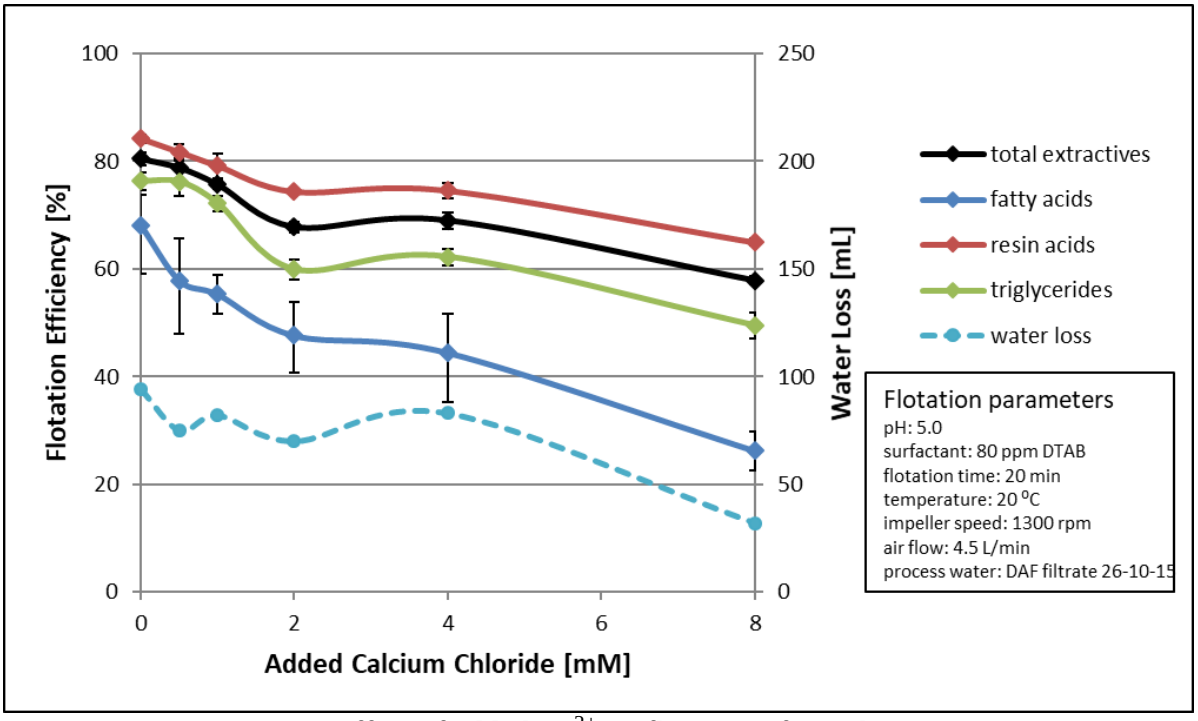


Figure 5-7 Effect of added Ca^{2+} on flotation of wood extractives

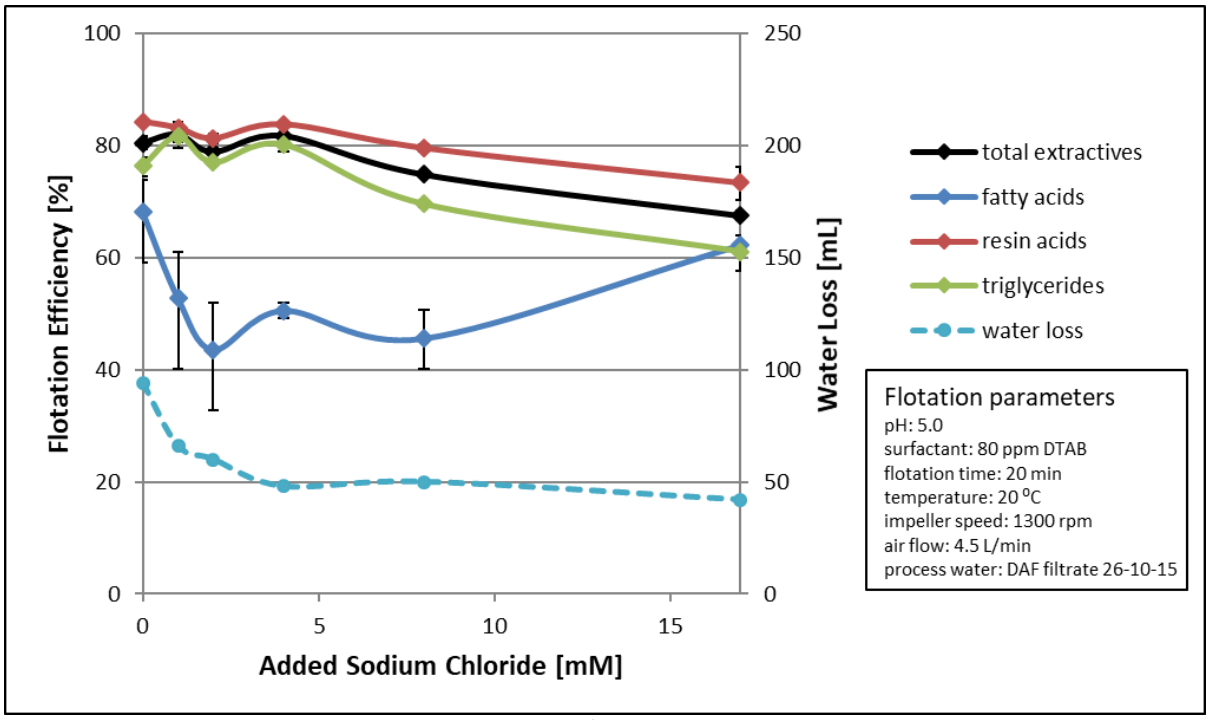


Figure 5-8 Effect of added Na^+ on flotation of wood extractives

A decrease in flotation efficiency was observed with increasing calcium carbonate addition (Figure 5-7). The trend applied to all extractive classes indicating an effect on colloid flotation most likely due to the known effect of electrolytes on the electrical double layer, compressing its range and reducing the zeta potential so that colloids and air bubbles would need to be closer together to experience an attractive force. Colloidal wood extractives are known to be stabilised by steric hindrance from wood polysaccharides found in TMP water [42, 46, 47]. This steric hindrance would presumably also keep colloids separated from air bubbles so they may not come close enough to experience an electrostatic attraction, particularly when the electrical double layer is compressed. Even so, the effect of calcium ions on flotation efficiency was not great, suggesting that the flotation rate is controlled by attachment of colloids to air bubbles which will occur to some extent through electrostatic attraction regardless of the magnitude. As attraction between the oppositely charged colloids and air bubbles reduces with electrolyte concentration, so too does the stabilising repulsion between the like charged colloids. This destabilisation is known to cause coagulation of colloids at high electrolyte concentration. Destabilisation can result in coagulation which may affect flotation by changing the size of wood extractive particles. Coagulation can occur

above the critical coagulation concentration (ccc) which has been reported as 7.8 mM for coagulation of *P. radiata* wood extractive dispersions by Ca^{2+} [54, 57]. This value is within the range studied of 0 - 8 mM especially considering the initial process water contained about 0.5 mM dissolved calcium. However, no obvious change in flotation efficiency was found at this concentration and no spontaneous coagulation was observed. This was most likely due to steric hindrance of wood polysaccharides which have been shown to stabilise wood extractive colloids against electrolyte induced aggregation [42, 46, 47].

The effect of added sodium chloride was not as extreme, but also led to reduced flotation efficiency over the range studied (Figure 5-8). The range was chosen to give a similar conductivity measurement to that of the added calcium range. The maximum calcium carbonate addition of 8 mM resulted in 2.27 mS/cm and the maximum sodium chloride addition resulted in 2.61 mS/cm compared to 0.75 mS/cm for flotation without addition. The effect of a monovalent cation such as Na^{+} is expected to be much less than a divalent cation like Ca^{2+} based on the Debye length dependence on valency. This is also reflected in the ccc which at 720 mM is two orders of magnitude higher than the Ca^{2+} ccc [54, 57].

5.2.3 Effect of dissolved organic wood polymers

The effect of dissolved organic wood polymers on flotation efficiency was studied by measuring flotation efficiency with extra organic material added to the process water. The material was extracted from pulp by the method detailed in Chapter 2.9. The orcinol method for determining dissolved carbohydrates was then used to give a measure of the concentration of wood polymers in process water before flotation. The flotation results are presented in Figure 5-9.

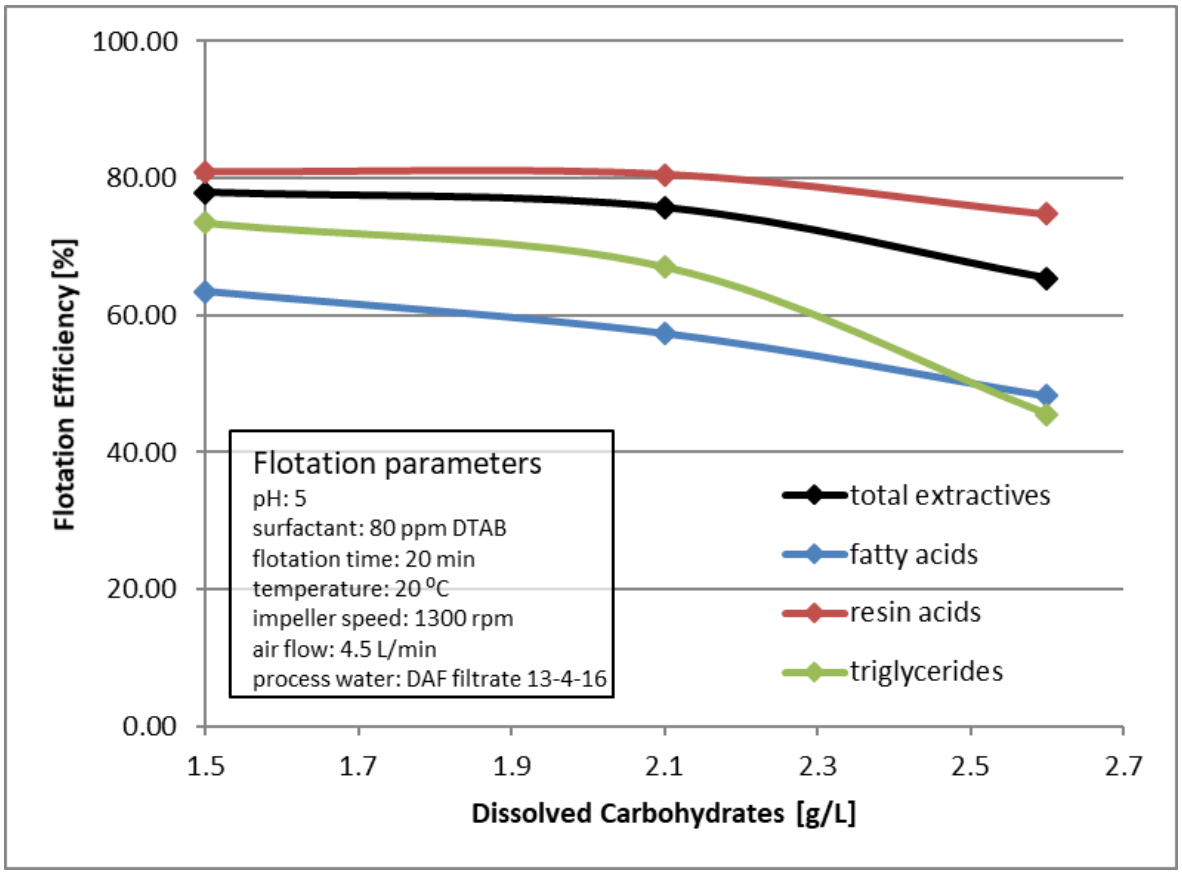


Figure 5-9 Effect of dissolved wood polymers on flotation of wood extractives

Additional dissolved organic wood polymers reduced the flotation efficiency of all extractive classes particularly the triglycerides, indicating an effect on colloid flotation most likely due to steric hindrance preventing the close proximity of colloids and air bubbles.

5.2.4 Effect of residual flocculant

The DAF filtrate process water used for flotation studies may have contained some residual flocculant which is normally added before DAF fibre recovery at the mill. The flocculant used is Nalco 6D16 which is a high molecular weight cationic poly-acrylamide (CPAM). Each molecule can form multiple bonds to fibre particles resulting in the formation of flocs which are more easily removed by DAF.

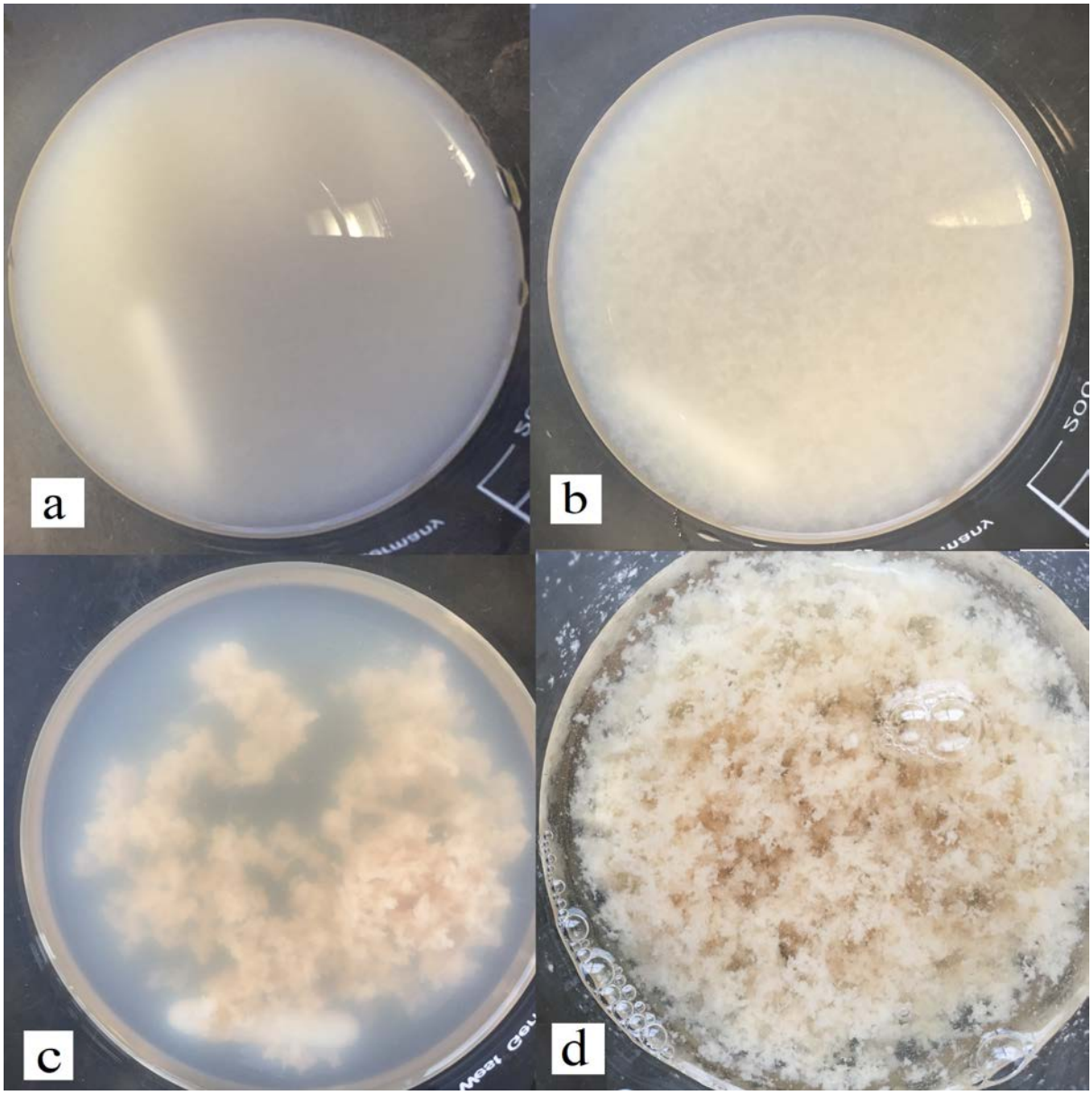


Figure 5-10 Appearance of process water with addition of flocculant a) 0.025 mL, b) 0.1 mL, c) 0.5 mL and d) 1.0 mL of flocculant to one litre of DAF filtrate (22-2-17).

To investigate the effect of this flocculant on flotation of wood extractives, different amounts of additional flocculant were added to the process water before flotation. Flocs were clearly observed in the process water after addition and mixing of the flocculant as shown in Figure 5-10.

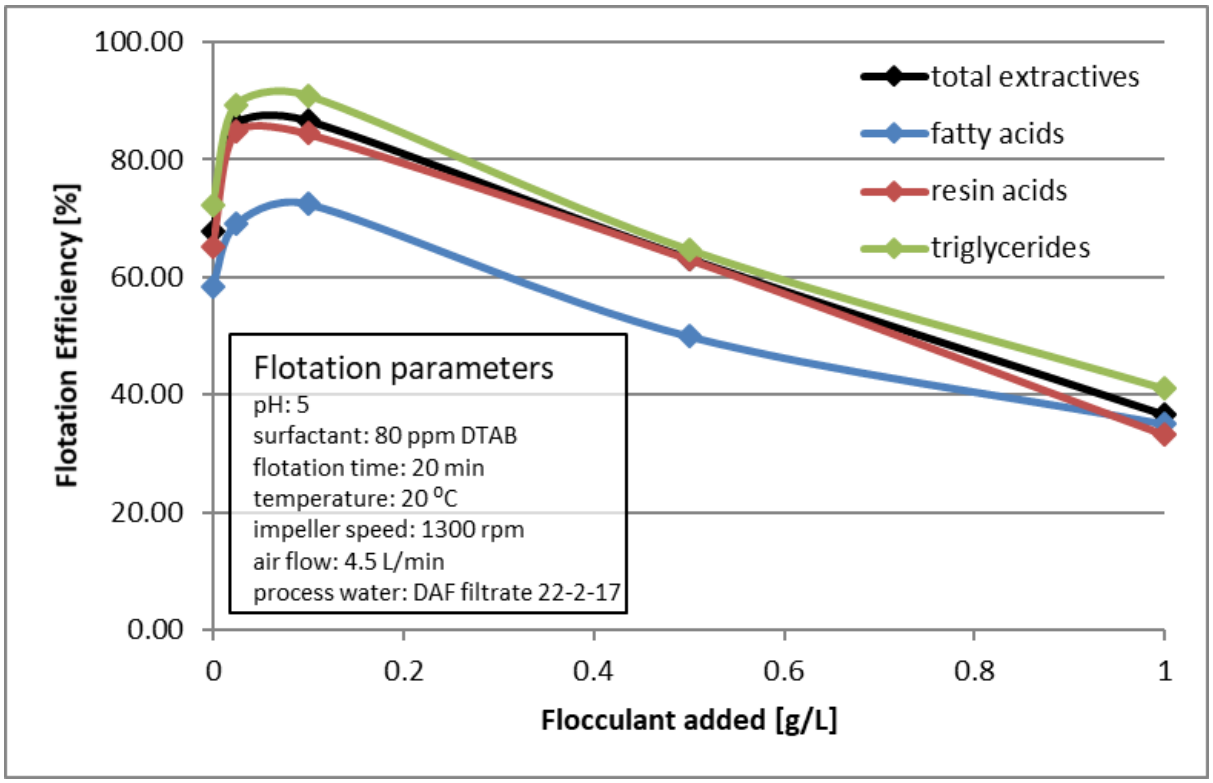


Figure 5-11 Effect of additional flocculant on flotation of wood extractives.

Flotation efficiency with each mixture is shown in Figure 5-11. Flotation efficiency was shown to be improved by the addition of a small amount of flocculant (less than 0.5 mL) but inhibited by larger amounts. It appeared that the smaller, lighter flocs formed at low concentrations were able to be floated but larger flocs were not. While it was not possible to easily determine the amount of flocculant in the process water as sampled from the mill, it is reasonable to assume that a residual amount was present and that this amount may have varied between batches of process water collected contributing to the variability in flotation efficiency between batches.

5.2.5 Different process water streams

The flotation method developed and optimised using water from Boyer DAF filtrate was then tested for efficiency with water from two streams from Norske Skog's other Australian paper mill in Albury, New South Wales. Process water was collected from two different streams

and characterised for comparison with the Boyer DAF filtrate water. The characterisation results are presented in Table 5-2.

Table 5-2 Characterisation of different process waters

	Boyer mill DAF filtrate 05/01/2016	Albury mill TMP effluent 02/06/2016	Albury mill PM/TMP DAF feed 02/06/2016
pH	6.0 ± 0.0	4.72	5.69
Conductivity [mS/cm]	0.50 ± 0.01	0.33	1.43
Ca [mg/L]	13	20.1	104
Dissolved Carbs [mg/L]	1.70 ± 0.03	1.392	3.058
fibre [%]	0.069 ± 0.003	0.9414	0.0862
fatty acids [mg/L]	18 ± 0	32	19
resin acids [mg/L]	202 ± 1	700	85
triglycerides [mg/L]	78 ± 1	189	35
total extractives [mg/L]	298 ± 1	921	140
dissolved phase	12 %	1 %	14 %
colloidal phase	74 %	36 %	32 %
fibre bound phase	13 %	63 %	54 %

Table 5-3 Fibre and extractives content of water used for flotation

	Boyer mill DAF filtrate 05/01/2016	Albury mill TMP effluent 02/06/2016 (supernatant)	Albury mill PM/TMP DAF feed 02/06/2016 (supernatant)
fibre [%]	0.069 ± 0.003	0.0328	0
fatty acids [mg/L]	18 ± 0	14 ± 0	13 ± 0
resin acids [mg/L]	202 ± 1	225 ± 35	40 ± 2
triglycerides [mg/L]	78 ± 1	99 ± 7	12 ± 2
total extractives [mg/L]	298 ± 1	338 ± 43	64 ± 4

Both Albury process waters were higher in fibre than the Boyer DAF filtrate (Table 5-2), so the centrifuge supernatant was used for flotation treatment. The fibre and extractives content in the resulting supernatant is displayed in Table 5-3. The Albury TMP effluent stream supernatant contained wood extractive concentrations similar to the Boyer DAF filtrate whereas the supernatant from Albury's PM/TMP DAF feed was substantially lower in extractives.

The flotation method proved effective for wood extractive removal from Albury mill process waters reducing the total extractives concentration by 82 ± 2% and 64 ± 6% in the TMP effluent stream and PM/TMP DAF feed stream respectively (Table 5-4). These are lower than the 95 ± 1% reduction in the Boyer DAF filtrate. Reasons for this may be predicted based on differences in characterisation results in Table 5-2. Albury process water had higher dissolved calcium levels which has already been shown to decrease flotation efficiency in Chapter 5.2.1-2.

Table 5-4 Flotation results for different process waters

	Boyer mill DAF filtrate 05/01/2016	**Albury mill TMP effluent 02/06/2016 (supernatant)**	**Albury mill PM/TMP DAF feed 02/06/2016 (supernatant)**
Flotation efficiency [%]			
	mean (of 5)	mean (of 2)	mean (of 2)
total extractives	**95** ± 1	**82** ± 2	**64** ± 6
fatty acids	**79** ± 2	**61** ± 11	**5** ± 0.2
resin acids	**97** ± 0.2	**86** ± 5	**77** ± 4
triglycerides	**93** ± 2	**76** ± 3	**56** ± 11

5.3 Conclusions

Flotation efficiency was found to be adversely affected by high ionic strength particularly due to calcium. This was most likely due to reduction in attraction and attachment between colloids and air bubbles due to compression of the electrical double layer and reduction in zeta potential. High levels of dissolved organic wood polymers also reduced flotation efficiency by keeping colloids and air bubbles apart by steric hindrance. Conductivity, dissolved calcium concentration and dissolved carbohydrates were also identified by linear regression analysis to be negatively correlated to flotation efficiency. Addition of flocculant to the process water improved flotation at low levels (100 mg/L) but decreased efficiency above 500 mg/L as the heavier flocs could not be floated. These three factors combined may explain the variation observed in flotation efficiency between batches.

The flotation method developed was shown to effectively remove extractives from process water collected from a second pulp and paper mill that processes *P. radiata* in combination with recycled pulp. The flotation efficiencies were lower however. This may be explained by the higher dissolved calcium concentrations.

Chapter 6 Recovery and separation of wood extract and surfactant

6.1 Introduction

Froth collected from the developed flotation method collapsed to form a brown cloudy liquid with settled sediment. It contained concentrated extractives (dissolved, colloidal, coagulated and fibre bound), fibre, and DTAB. A method was sought to recover the extractives as a natural product and the DTAB for reuse.

Methods investigated were ultra-filtration and solvent extraction. Although, there has been no documented recovery of extractives from flotation in the literature, both ultra-filtration and solvent extraction have been used for removing wood extractives from other sources.

Ultra-filtration has been investigated for purification of TMP process water [134-138]. A major obstacle to the efficacy of such methods is fouling of the filtration membrane by components in the process water with wood extractives and polysaccharides reported as contributors [134-137]. Persson et al. fractionated TMP process water by different levels of filtration [137]. Suspended matter was mostly retained by a drum filtration system, extractives by micro-filtration, hemicelluloses by ultra-filtration and lignin by nano-filtration. Puro et al. evaluated the fouling potential of wood extractives and found resin and fatty acids to be the major contributors [136]. Singh et al. used NaOH and SDS to pre-treat TMP process water for ultra-filtration [135]. SDS treatment was most effective at reducing irreversible fouling presumably by solubilising fatty and resin acids [135]. Thevander et al. examined fouled membranes and identified glucan rich polysaccharides as the major contaminant responsible for irreversible fouling [134]. Lipophilic extractives such as resin and fatty acids were largely removed by micro-filtration pre-treatment [134]. Rudolph et al. investigated enzyme and alkaline treatments for cleaning fouled membranes and found that the permeability could be restored though extractives were not completely removed from the membranes. In summary, it appears that resin and fatty acids have the potential to foul membranes and contribute to the irreversible fouling of polysaccharides but can be removed by SDS or micro-filtration pre-treatments.

Solvent extraction is routinely used in the sample preparation for analysis of wood extractives [139]. Lipophilic wood extractives are soluble in a variety of organic solvents and common solvents used to extract them include MTBE, acetone, hexane, diethyl ether, ethyl acetate, and dichloromethane [1, 4, 139].

Efficient removal of wood extractives by both solvent extraction and ultra-filtration relies on insolubility of the extractives in water which is dependent on pH and the choice of the immiscible solvent. Effective separation of DTAB from the extractives will depend on the solubility of DTAB in water and insolubility in the immiscible solvent.

The solubility of quaternary ammonium salts including DTAC in various solvents was studied by Reck et al [140]. As would be expected for salts, the compounds were generally more soluble in more polar solvents. The exceptions being that they were also soluble in the chlorinated solvents tested: chloroform and carbon tetrachloride. This was explained by the potential for hydrogen bonding between the solvent and solute. DTAC was found to be essentially insoluble in both *n*-hexane and ethyl acetate reporting solubilities of < 0.2 g in 100 g and < 0.39 g in 100 g respectively at 95°C. Octodecyltrimethyl ammonium chloride was found to be more soluble in the non-polar solvents than DTAC which is presumably due to its longer hydrocarbon chain. A later study reported solubility for CTAB of less than 0.1 g/L in toluene, MTBE and ethyl acetate [141]. The partitioning of various surfactants between the solvent and water phase was also examined and partition coefficients determined at different extraction conditions. CTAB did not measurably partition into toluene, MTBE or ethyl acetate at pH 2, 7 or 10, and the partition coefficients were reported as 0.00 for each of these conditions [141]. Addition of 1 M KCl to the extraction solution did not change this and nor did addition of 5% methanol or 30% heptane to the organic phase [141].

6.2 Results and Discussion

6.2.1 Residual DTAB

To determine the fate of DTAB during flotation, the process water before, during and after flotation was analysed. Samples of the water were taken at intervals during flotation and

analysed for DTAB concentration by Noel Davies at the CSL using a UPLC-MS method detailed in Chapter 2.8. The concentration of extractives was also determined from GC analysis. The results are presented in Figure 6-1.

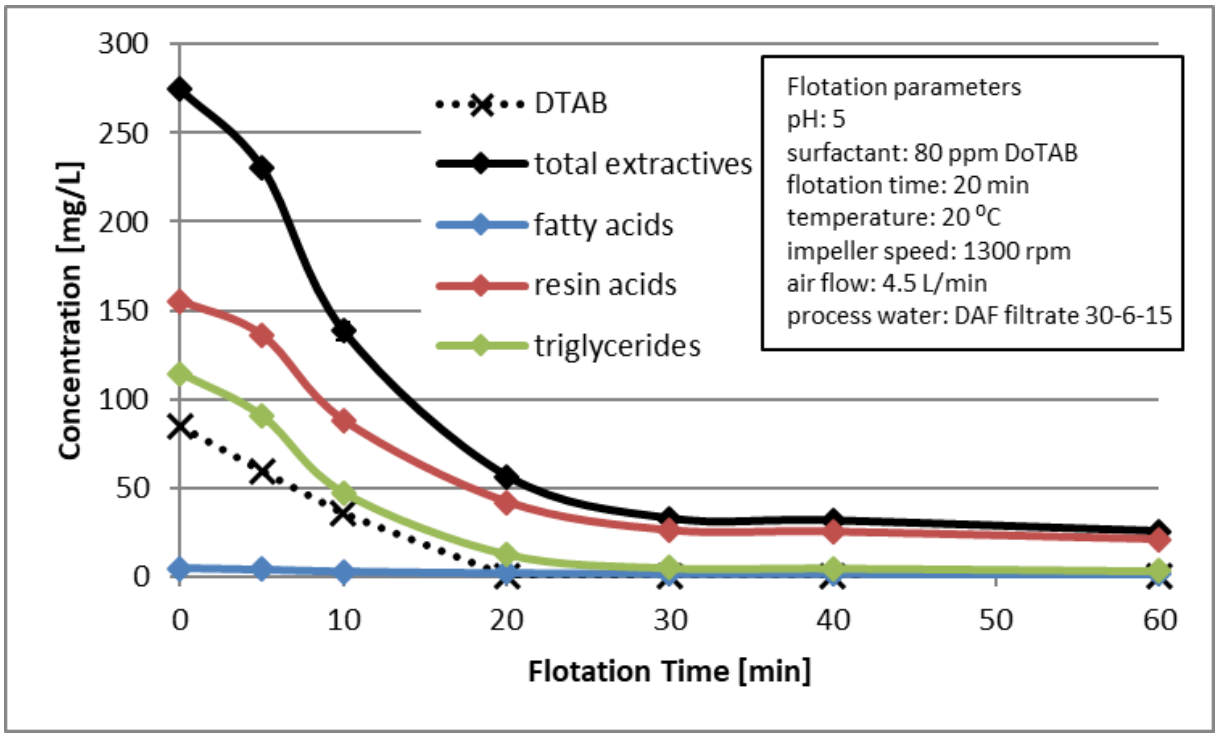


Figure 6-1 Concentration of DTAB and extractives during flotation

The DTAB concentration dropped to zero by 20 min which is also the time point at which extractives removal began to drop off. Therefore, it is concluded that the DTAB was removed in the froth with the extractives. The DTAB concentration did appear to drop more suddenly to zero whereas the extractives concentrations gradually declined to a minimum. This can be seen more clearly in Figure 6-2 which presents the same data in a different way showing the increase in removal efficiency with flotation time. The sharper change in the DTAB trace compared to the extractives may be due to losses during sample preparation caused by the surface activity of DTAB which gives it a propensity to adhere to surfaces and particles. Such losses would have a greater effect on the measurement of low concentrations. Therefore, the true decline in DTAB concentration may follow a curve like the extractives.

Since the DTAB additive was removed during flotation, water treated by this method should be suitable for recirculation to other mill processes with effectively no residual DTAB.

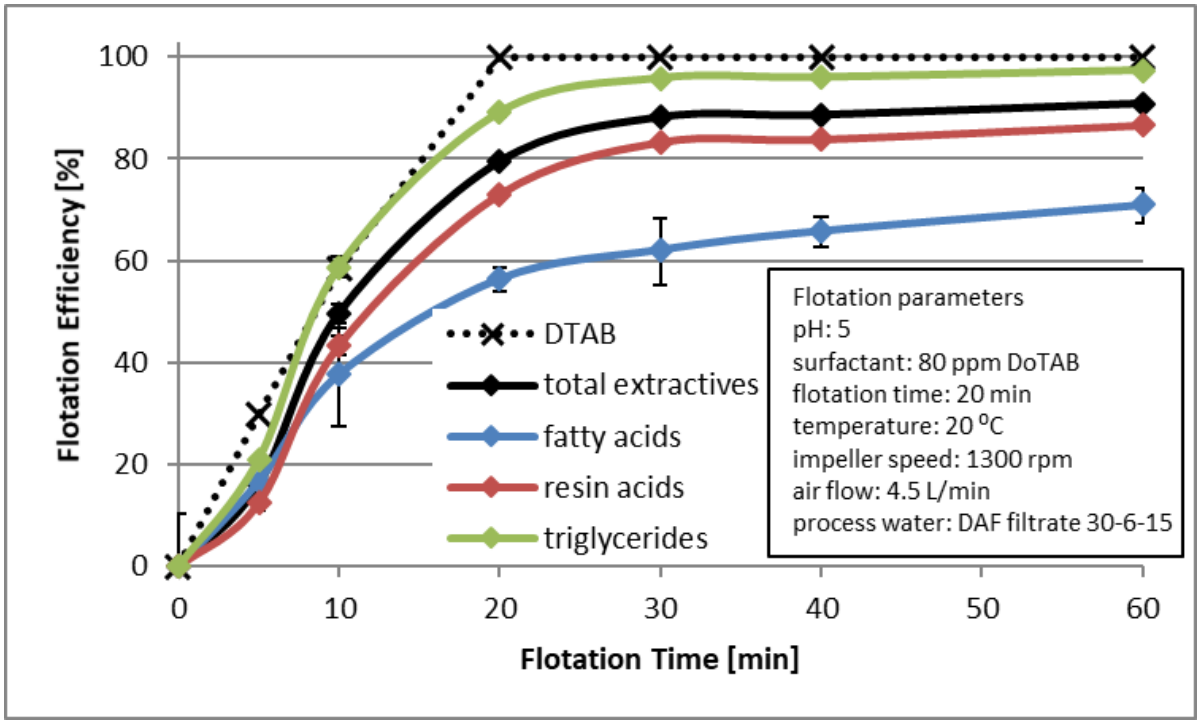


Figure 6-2 Flotation efficiency of DTAB and extractives during flotation

Sample preparation for DTAB analysis required dilution and filtration through a 0.45 µm filter to remove any particles. DTAB is very soluble in water at the concentrations used and its cmc is about 4 g/L [109, 110] so it should remain in the aqueous phase during filtration. However, its surface activity gives it the propensity to adhere to surfaces. It was found that DTAB was lost during filtration dependent on the wood extractives concentration. This was discovered after preparing process water samples by two different methods: one in which filtration was performed before dilution and the other in which filtration was done after dilution. Thus, different levels of wood extractives were present during the filtration step. This order of sample preparation affected the results as presented in Table 6-1.

Table 6-1 Effect of filtration on DTAB analysis

DAF filtrate (13/04/2016) with 80 mg/L DTAB Sample:	1	2	3	4
order of procedures	filtration then dilution		dilution then filtration	
dilution factor	50	100	50	100
wood extractives concentration during filtration [mg/L]	172	172	3.4	1.7
Result: DTAB concentration [mg/L]	50.68	45.79	74.30	109.83

The DTAB concentrations presented in the table have been corrected for the dilution factor to give the concentration in the original sample. Samples 1 and 2 which were filtered prior to dilution gave lower DTAB results, whereas samples 3 and 4, filtered after dilution gave higher DTAB readings. This appears to indicate interaction between the DTAB and wood extractives, something not reflected in earlier results which showed no change to zeta potential of wood extractive colloids with DTAB addition (Figure 3-8). A possible explanation is that interaction is minimal in solution but is induced by the filtration process due to the proximity of colloids collected on the filter with DTAB passing through. It was concluded that filtration of samples should be the final step in sample preparation (as was the case for the results presented in Figure 6-1 and Figure 6-2) and that the method may not be suitable for preparation of samples with high extractives content.

6.2.2 Ultra-filtration

Ultra-filtration was investigated as a method for the separation of DTAB and extractives from the concentrate removed as froth during flotation. The froth concentrate was collected from duplicate flotation batches performed at optimal conditions: 60 °C, pH 5, 80 mg/L DTAB, 1300 rpm impeller speed and 4.5 L/min airflow. The froth concentrate was filtered through a regenerated cellulose filter (Millipore, YM3 NMWL = 3000) at 300 kPa pressure. The filtrate was collected and analysed for DTAB and extractives content. It was firstly dried, and then extracted with acetone to recover the extractives, which were analysed by GC. The filtration

process was slow, but the extractives appeared to be collected efficiently on the filter with no observed membrane fouling or decrease in the filtration rate. The amounts of extractives recovered from the filter and from the filtrate are recorded in Table 6-2.

Table 6-2 Ultra-filtration of the froth concentrate

	duplicate 1		**duplicate 2**	
froth concentrate volume [mL]	103		81	
ultra-filtration time [hr]	1.5 hr		2.5 hr	
volume of filtrate [mL]	84		64	
extractives recovered from filter	**mass [mg]**	**proportion**	**mass [mg]**	**proportion**
fatty acids	9.3 ± 0.4	97%	10.4 ± 0.1	98%
resin acids	92 ± 5	99.6%	115 ± 1	99.8%
triglycerides	45 ± 2	100.0%	50.9 ± 0.1	100.0%
extractives recovered from filtrate	**mass [mg]**	**proportion**	**mass [mg]**	**proportion**
fatty acids	0.28 ± 0.01	3%	0.22 ±0.01	2%
resin acids	0.35 ± 0.01	0.4%	0.24 ± 0.01	0.2%
triglycerides	0.02 ± 0.01	0.0%	0.01 ± 0.01	0.0%
DTAB recovered from filtrate [mg]	8 ± 1		6 ± 1	

The extractives were mostly retained by the filter with more than 99% of resin acids and triglycerides retained and more than 97% of fatty acids retained. These percentages are based on the total amounts found both on the filter and in the filtrate. Only very low concentrations of extractives were observed in the filtrate. Less than 3% of fatty acids and less than 1% of resin acids and triglycerides were found in the filtrate. This was expected as the mixture had a pH 5.0 at which the extractives have very low solubility in water. DTAB, on the other hand,

was expected to remain in the filtrate due to its high solubility in water, as indicated by its cmc of 13-14 mM (4 000 mg/L) [109, 110], and molecular weight (308 g/mol) much less than the 3000 g/mol pore size of the filter. However, the amount of DTAB found in the filtrate is only a small percentage of the expected value. The amount of DTAB added to each 1 L flotation batch was 80 mg and the majority of this should be collected in the froth concentrate as explained in Chapter 6.2.1. Hence, a maximum of 80 mg was expected in the filtrate after ultra-filtration of the froth concentrate. The amount found (presented in Table 6-2) was only 8 ± 1 and 6 ± 1 mg for each of the duplicate filtrations, that is, only about 10% of the expected amount. This indicates that the DTAB must be retained on the filter during ultra-filtration. Its interaction with the extractives may have prevented its dissolution in water and removal with the filtrate. Thus, although the evidence shows minimal interaction between wood extractive colloids and DTAB before flotation (Figure 3-8), significant interaction may occur during and after flotation. This could be due to a stepwise process in which DTAB most readily adsorbs to the bubble surfaces initially, then attaches to wood extractive colloids by electrostatic attraction, enabling more gradual and irreversible interaction which forms insoluble complexes. This would explain the observed agglomeration of extractives in the collected froth. Korpela observed similar agglomeration of resin particles after flotation of TMP water and attributed it to the high localised concentration of resin particles after drainage and collapse of froth [85]. A similar mechanism was also described by Allen [142] for deposit formation. Studies of mixed surfactant systems show that insoluble complexes form at higher concentrations especially in 1:1 ratios of the cationic and anionic surfactant [127, 128]. These conditions may occur during froth drainage and collapse, and in the froth concentrate. Because this trial of ultra-filtration did not effectively separate DTAB from the extractives, it was not pursued further.

6.2.3 Centrifugation

It was observed that during flotation, wood extractives appeared to coagulate in the froth and then settle in the collected froth concentrate. This is a good explanation for the current work since the extractives did not coagulate on addition of DTAB but only after flotation.

Considering this coagulation, it seemed reasonable that the extractives might be removed by centrifugation. The results of centrifugation of froth concentrate (from flotation of DAF filtrate 9-Apr-2015) are presented in Table 6-3. Samples of 5 mL volume were centrifuged in duplicate at 500 G for 10 min using an Eppendorf 5810.

Table 6-3 Wood extractives removed from froth concentrate by centrifugation

	Resin acids	Fatty acids	triglycerides	Total extractives
Sample [mg/L]	920 ± 10	55 ± 1	590 ± 20	1570 ± 30
% in pellet	44.4 ± 0.3 %	38.1 ± 0.2 %	37.8 ± 0.3 %	41.7 ± 0.3 %

Centrifugation removed 41.7 ± 0.3 % of extractives (as part of the pellet), leaving more than half the extractives in the supernatant which still appeared turbid. As such, centrifugation was not considered an effective method for recovery of the wood extractives.

6.2.4 Solvent extraction

6.2.4.1 Comparison of different solvents

A range of solvents were tested for extraction of the wood extractives from the froth concentrate. These were evaluated based on the formation of a clear solvent/water interface, recovery of extractives, and weight of final extract. An initial experiment which compared the solvents MTBE, hexane, toluene, ethyl acetate and heptane found that only the less polar hexane, heptane and toluene formed a clear solvent layer that was easily removed from the aqueous layer. The solvent-aqueous interfaces are shown in Figure 6-3. MTBE and ethyl acetate produce a cloudy brown solvent layer indicating the presence of suspended solids which may be fibres or coagulated material. Toluene produced a very thick opaque layer at the interface, but some clear solvent was able to be removed from the top. Hexane and heptane produced a layer of brown material at the interface though with the largest clear solvent layer above. Hence only these three solvents were used to further investigate the extraction efficiency.

Figure 6-3 Solvent-water interface with different solvents: 1-MTBE, 2-hexane, 3-toluene, 4-ethyl acetate, 5-heptane

Froth was collected from seven flotation batches performed at 20°C, pH 5.0, with 80 mg/L DTAB, 4.5 L/min airflow, 1300 rpm impeller speed and using process water from DAF filtrate 21-9-17. The collected froth was combined and analysed by GC. It contained 77.7 ± 0.4 mg/L fatty acids, 808 ± 8 mg/L resin acids and 475 ± 10 mg/L triglycerides. A double solvent extraction was performed in duplicate using each solvent according to the method described in Chapter 2.11. The results are presented in Table 6-4.

Table 6-4 Solvent extractions

	toluene	**heptane**	**hexane**
extract weight [mg/100g froth]	94 ± 1	108 ± 3	106 ± 1
proportion identified by GC (fatty acids, resin acids + triglycerides)	37 ± 1 %	59 ± 1 %	54 ± 3 %
recovery of extractives			
fatty acids	27 ± 2 %	34 ± 1 %	32 ± 1 %
resin acids	33 ± 1 %	68 ± 2 %	57 ± 3 %
triglycerides	13 ± 1 %	14 ± 1 %	17 ± 3 %
total	26 ± 1 %	47 ± 1 %	42 ± 3 %
extractives in aqueous layer			
(fatty acids, resin acids + triglycerides)	7.1 ± 0.2 %	3.13 ± 0.01 %	4.2 ± 0.8 %
DTAB in aqueous layer [mg/L]	223 ± 1	201 ± 1	199 ± 4

Heptane gave the highest extract yield of 108 ± 3 mg per 100 g of froth concentrate. It was also the most concentrated in the components identifiable by GC (fatty acids, resin acids and triglycerides) with 59 ± 1 % of the weight identified in these classes. By contrast the toluene and hexane extracts contained less of these components and a larger unidentified component. The highest total recovery of resin acids, fatty acids and triglycerides was obtained by heptane extraction which gave 47 ± 1 % recovery. Analysis of the aqueous layer by GC revealed only 3.13 ± 0.01 % remaining in the aqueous layer. This means about 50 % of extractives have not been accounted for in either the solvent or aqueous layer. They must therefore, have been lost to the layer observed at the interface.

Analysis of DTAB in the aqueous layer revealed around 200 mg/L for each extraction which is much less than the expected concentration of around 800 mg/L. This concentration was expected based on the 80 mg/L added for froth flotation which was previously shown to be collected with the froth. The DTAB levels in the solvent were not measured but were assumed to be very low in these non-polar solvents since DTAB is an ionic salt with very low solubility in non-polar solvents [140, 141]. Thus, as a substantial amount of DTAB was unaccounted for, it may have been lost to the layer at the interface.

It was hypothesised that interaction between the DTAB and wood extractives to form insoluble complexes caused them to remain at the interface rather than partitioning to either the solvent or aqueous phase.

6.2.4.2 DTAB effect on solvent extraction

To determine the effect of DTAB on solvent extraction, extractions were performed with and without DTAB. This was done using a model froth mixture as it was not possible to collect the froth from flotation without DTAB. The model froth was prepared by mixing oleic acid (Fluka ≥99%), abietic acid (Acros Organics 85%) and glyceryl trioleate (Sigma 65%) to represent the fatty acids, resin acids and triglycerides components, respectively, of the froth concentrate. These extractives were dissolved in TBME to accurately dispense the required amount into each sample tube. The TBME was then evaporated and 25 mL of either water or

an 800 mg/L DTAB solution was added to make up the model froth concentrate volume. The concentration of this model froth was made up to 130 mg/L oleic acid, 850 mg/L abietic acid and 580 mg/L glyceryl trioleate. Duplicates extractions were performed with both toluene and hexane using 2 times 10 mL of solvent according to the method described in Chapter 2.11. The results are displayed in Table 6-5 and Table 6-6.

Table 6-5 Effect of DTAB on hexane extraction of model froth

	with DTAB	**without DTAB**	**blank**	**control**
mass added [mg]				
extractives	50.3	50.3	0	0
DTAB	20.2	0	0	20.2
mass recovered [mg] (extract weight)	24 ± 1	34.1 ± 0.5	3.4 ± 0.0	3.3 ± 0.1
extractives recovery (by mass)	42 ± 2 %	61 ± 1 %		
extractives recovery (by GC)	72 ± 4 %	98 ± 1 %		

Table 6-6 Effect of DTAB on toluene extraction of model froth

	with DTAB	**without DTAB**	**blank**	**control**
mass added [mg]				
extractives	50.3	50.3	0	0
DTAB	20.2	0	0	20.2
mass recovered [mg] (extract weight)	27.2 ± 0.1	44.9 ± 0.3	4.5 ± 0.1	4.3 ± 0.2
extractives recovery (by mass)	45.2 ± 0.1 %	80.3 ± 0.6 %		
extractives recovery (by GC)	60.8 ± 0.2 %	103.3 ± 0.2 %		

The extract obtained was weighed and compared with the expected weight to give the recovery. Duplicate blank extractions were performed using only solvent and deionised water. The small extract weight obtained from the blanks of 3.4 ± 0.0 mg for hexane and 4.5 ± 0.1 mg for toluene was attributed to impurities in the solvent and was used to correct the sample extract weights for calculation of the extractives recovery. Duplicate control samples were also performed with no added extractives but with the DTAB. These gave extract weights no greater than the blanks which indicates that DTAB is not extracted into the solvent.

Recovery of extractives was significantly higher in the absence of DTAB for both hexane and toluene extraction. Only 42 ± 2 % of extractives were recovered by hexane extraction with DTAB present whereas 61 ± 1 % was recovered without DTAB (Table 6-5). The difference is even greater for the toluene extractions with 45.2 ± 0.1 % recovery with DTAB and 80.3 ± 0.6 % without DTAB (Table 6-6). This indicates that DTAB prevented the extractives from partitioning to the solvent phase.

Two problems were identified during this experiment. First, due to the high concentration of extractives, the extractives in the model froth did not disperse evenly in the solution but attached to walls of the sample tube. This should not have had a large effect though as shaking during solvent extraction should have ensured sufficient opportunity for the extractives to partition into the solvent phase. Second, the concentrations of abietic acid and glyceryl trioleate were lower than expected, most likely due to oxidation of the compounds during storage. Due to this the recovery based on mass includes recovery of the oxidation products as well as the resin acid and triglyceride. The recovery of extractives based on GC analysis was also calculated and gave higher recovery but showed the same trends as the mass measurements. Close to 100% of extractives present were recovered in the absence of DTAB but only 72 ± 4 % was recovered by hexane (Table 6-5) and 60.8 ± 0.2 % by toluene extraction (Table 6-6). These results again indicate that the presence of DTAB interferes with solvent extraction.

It is concluded that interaction between the extractives and DTAB prevents their dissolution in either the solvent or water phase. This may explain the previously observed losses in both extractives and DTAB recovery during solvent extraction. The extractives and DTAB most likely remain in the layer observed at the interface.

6.2.4.3 Optimal pH

As the electrostatic interaction between DTAB and extractives is affected by pH, it would be expected that both extractives recovery and DTAB recovery may also be affected by pH. The proportion of ionised extractives increases with pH which also increases their solubility in water. Increased ionisation of extractives to form negatively charged anions should increase their interaction with the positively charged DTAB cation, hindering their removal in the aqueous phase. Alternatively, their increased water solubility may improve their removal in the aqueous phase. To investigate this, extractions of froth concentrate were performed over a pH range of 2.6 to 10.3. Froth was collected from five flotation batches performed at optimal conditions (60°C, pH 5.0, with 80 mg/L DTAB, 4.5 L/min airflow, 1300 rpm impeller speed) and using process water from DAF filtrate 23-1-18. The collected froth was combined and analysed by GC. It contained 83 ± 1 mg/L fatty acids, 1462 ± 5 mg/L resin acids and 722 ± 4 mg/L triglycerides. Duplicate samples of the froth concentrate were allocated for each pH value and the pH adjusted prior to extraction. A double heptane extraction was then performed according to the method described in Chapter 2.11. The resulting extracts were weighed and analysed by GC for fatty acids, resin acids and triglycerides. Their compositions are shown in Figure 6-4.

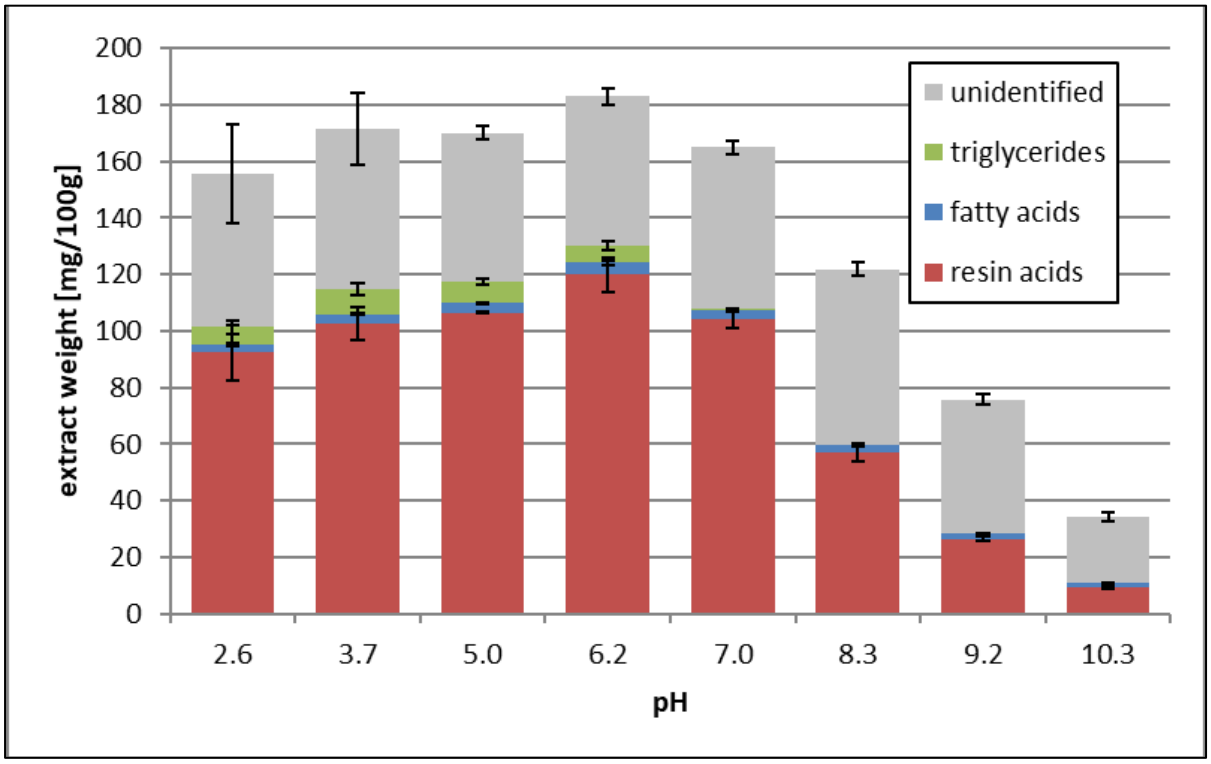


Figure 6-4 Composition of extract obtained by heptane extraction at different pH

The highest weight of extract was obtained at pH 6.2 which gave 183 ± 3 mg of extract per 100 g of froth concentrate. This extract also contained the most resin acids. Above pH 6 the amount of extract declined indicating that the extractives partitioned less into the heptane phase which is consistent with their increased ionisation and water solubility. Increased electrostatic interaction with DTAB may also contribute by preventing dissolution in heptane. Below pH 6 a more gradual decline in recovery was observed which may be attributed to increased hydrophobic interaction with DTAB. The unidentified portion of the extract contains substances that were extracted but not identified by GC as either fatty acids, resin acids or triglycerides. These most likely include sterols, steryl esters, waxes, and oxidised compounds [1].

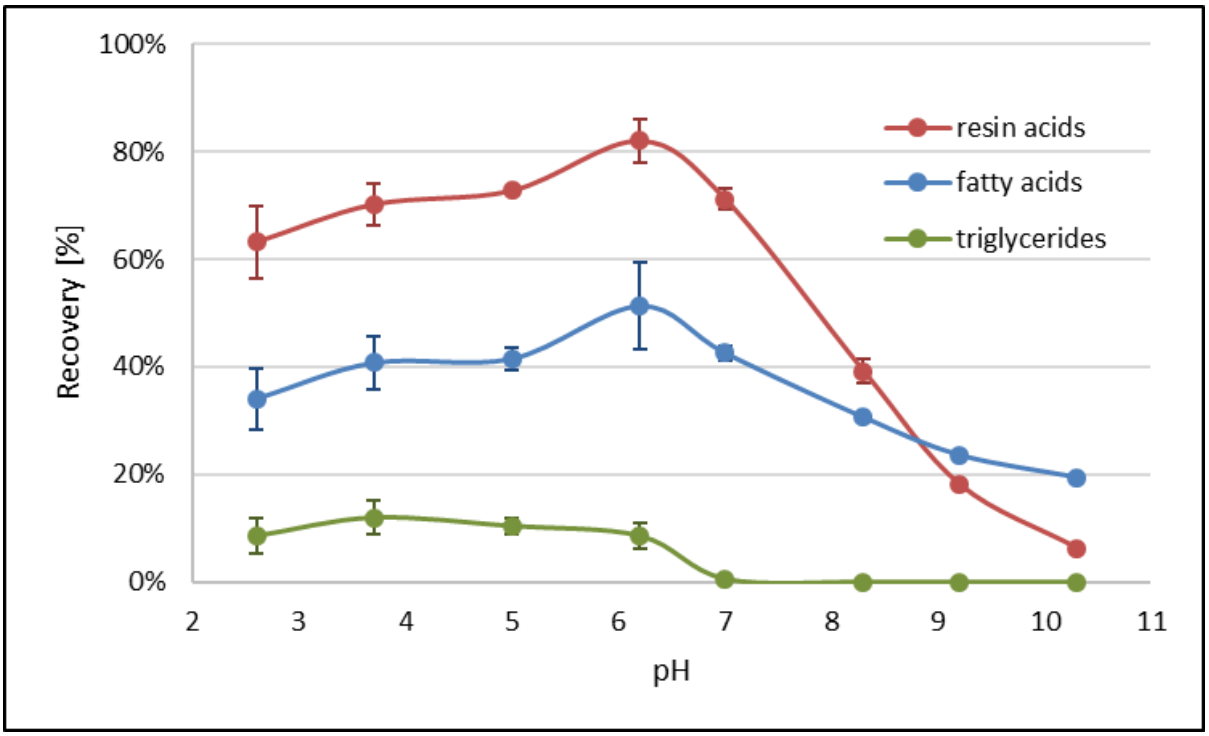


Figure 6-5 Extractives recovery by heptane extraction at different pH

Recovery of the resin acids, fatty acids and triglycerides was calculated from the concentration of these components in the froth concentrate and is shown in Figure 6-5. Recovery of fatty and resin acids peaked at around pH 6 with 82 ± 4 % of resin acids and 51 ± 8 % of fatty acids recovered. The triglycerides on the other hand were poorly recovered with less than 20 % recovery across the full pH range. Being neutral molecules, the triglycerides have lower solubility in water than the fatty and resin acids and should partition into the heptane. However, the low recovery by heptane extraction shows this was not the case. It is believed that the triglycerides must have remained at the solvent interface.

The aqueous phase was also analysed for DTAB and the results are shown in Figure 6-6.

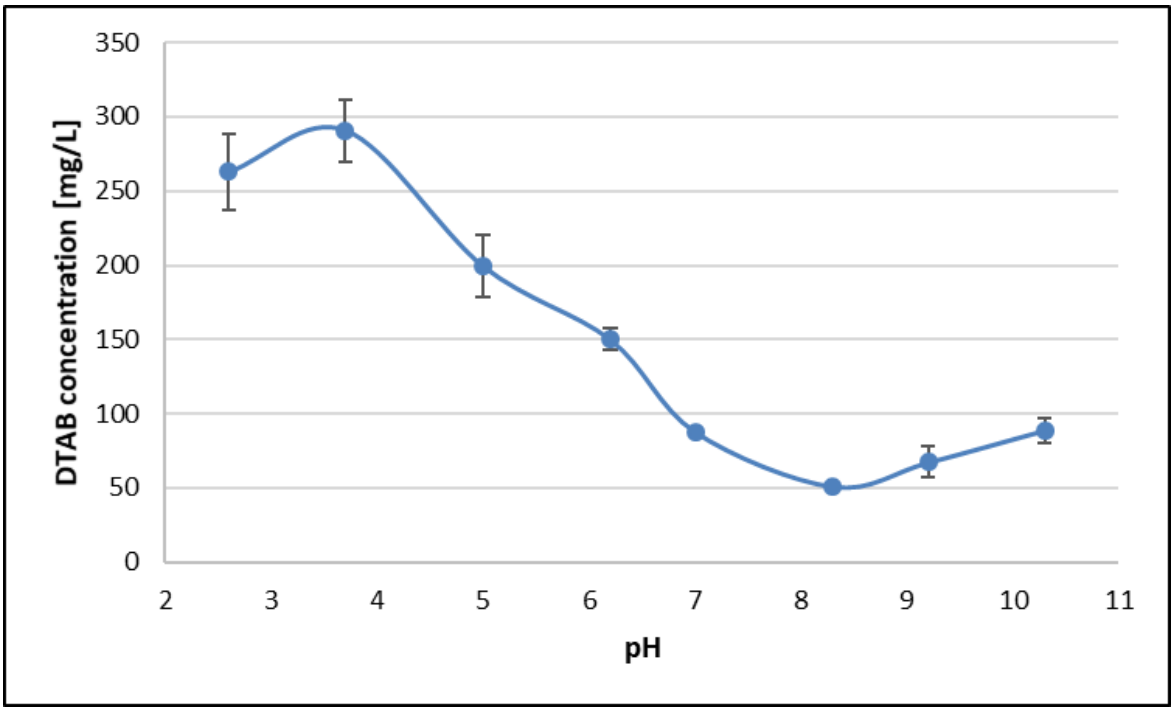


Figure 6-6 DTAB in the aqueous phase after heptane extraction

The DTAB concentration was low at alkaline pH and higher at acid pH, with the maximum concentration of 290 ± 20 mg/L at pH 3.7. This is a similar trend to that of the resin and fatty acids recovery suggesting an interaction between them and DTAB. However, the maximum DTAB concentration was well below the expected concentration of around 800 mg/L. Therefore, even at the optimal extraction pH, some DTAB was retained by either the solvent phase or at the interface. According to the literature on solubility and partition behaviour of cationic surfactants, DTAB should not partition into the organic solvent phase [140, 141]. As such, it is likely to be retained in the interface layer with the triglycerides. Interaction between DTAB and triglycerides must be a hydrophobic one since triglycerides are neutral molecules.

In conclusion, the optimal pH for recovery of wood extractives by heptane extraction is around pH 6 at which the maximum recovery of the resin and fatty acids was observed. Recovery of triglycerides and DTAB was low even at this pH suggesting a hydrophobic interaction prevented them from partitioning into either the organic solvent or water phase but retained them at the solvent-water interface.

6.2.4.4 Solvent polarity and solvent mixture ratio

Only low polarity solvents are immiscible with water and therefore suitable for solvent extraction from water. To investigate a wider range of solvent polarity, dry extractions were performed. To do this, water was evaporated from the froth concentrate by drying in an oven at 60°C for 25 hrs. The dried froth concentrate was then soaked in the test solvent and filtered through Whatman #540 filter paper to remove solids. The solvent was then evaporated to obtain the final extract which was analysed for extractives by GC.

Table 6-7 Solvent polarity and extraction of dry froth concentrate

	acetone	**ethyl acetate**	**MTBE**	**toluene**	**heptane**	**hexane**
relative polarity [143]	0.355	0.228	0.124	0.099	0.012	0.009
colour of filtrate	orange-yellow	yellow	pale yellow	pale yellow	almost colourless	very pale yellow
extract weight [g/100g of froth]	454	337	315	313	278	266
recovery of extractives						
fatty acids	55 %	66 %	62 %	60 %	59 %	58 %
resin acids	65 %	82 %	77 %	72 %	75 %	59 %
triglycerides	61 %	72 %	68 %	71 %	70 %	56 %
total	**62 %**	**76 %**	**71 %**	**69 %**	**71 %**	**57 %**
unidentified component of extract	46%	50%	47%	47%	40%	68%

The froth concentrate was collected from five flotation batches performed at 20°C, pH 5.0, with 80 mg/L DTAB, 4.5 L/min airflow, 1300 rpm impeller speed and using process water from DAF filtrate 13-7-17. The collected froth was combined and analysed by GC. It contained 63 ± 11 mg/L fatty acids, 1449 ± 18 mg/L resin acids and 859 ± 23 mg/L triglycerides. Each extraction was performed on 10 g of the froth concentrate. Duplicates were not performed in this preliminary study. The results are presented in Table 6-7.

There was a clear trend in extraction results with polarity of the solvent. The more polar solvents gave a greater extract yield with a maximum 454 mg per 100 g of froth for acetone. The filtrate and extract were also more highly coloured for the more polar solvents, ranging from orange-yellow using acetone, to almost colourless, or very pale yellow with heptane and hexane respectively. The extract weight and colour did not reflect the fatty acid, resin acid and triglyceride recovery however, as the highest recovery of 76% was obtained using ethyl acetate followed by MTBE and heptane at 71%. This means that extra material was extracted which is reflected in the percentage of unidentified component in the extract and was lowest for heptane at 40%. Therefore, extraction with heptane gave the purest extract but extraction with ethyl acetate gave the highest recovery of the measured extractives.

A method for altering the polarity of a solvent is to mix it with a second solvent of different polarity. Since ethyl acetate and heptane gave good dry extraction results, and have a difference in polarity, these two solvents were used to optimise a solvent mixture for liquid/liquid extraction from the froth concentrate.

Froth was collected from twenty-one flotation batches performed at optimal conditions (60°C, pH 5.0, with 80 mg/L DTAB, 4.5 L/min airflow, 1300 rpm impeller speed) and using process water from DAF filtrate 23-1-18. The collected froth was combined and analysed by GC. It contained 91 ± 2 mg/L fatty acids, 1484 ± 2 mg/L resin acids and 600 ± 2 mg/L triglycerides. The froth concentrate was adjusted to pH 6 which was the previously determined optimal pH for heptane extraction. A double solvent extraction was then performed in duplicate using each solvent mixture according to the method described in Chapter 2.11. The 100% ethyl acetate extraction mixture developed a very thick emulsion layer which prevented separation of the solvent layer so these samples were discontinued. The results are presented in Figure 6-7 and Figure 6-8.

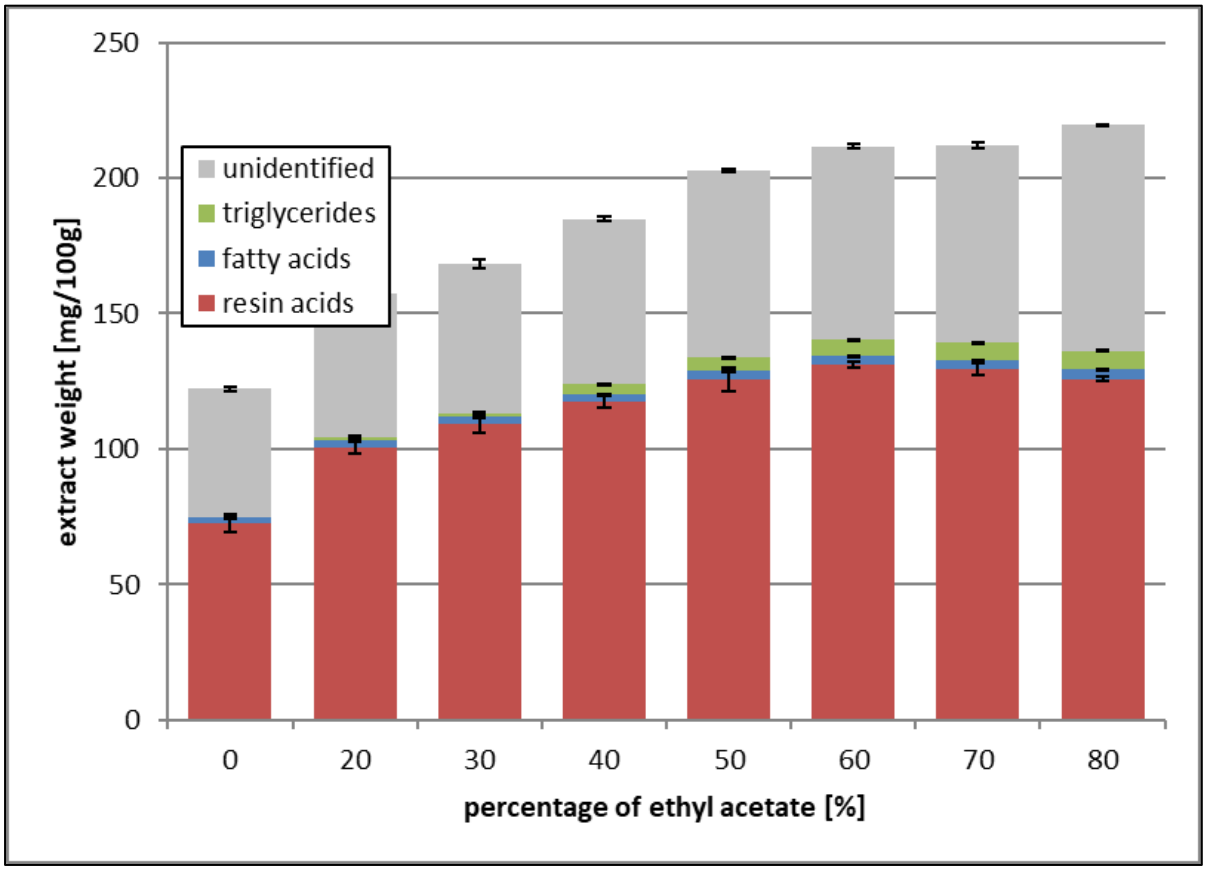


Figure 6-7 Composition of extracts obtained by solvent extraction with heptane/ethyl acetate mixtures

As with the dry extractions, the ethyl acetate extraction resulted in a higher extract yield of 261 ± 10 mg per 100 g of froth concentrate compared to heptane which yielded 122 ± 4 mg. The yield of measured extractives components (resin acids, fatty acids and triglycerides) was also higher for the ethyl acetate extraction which gave a total of 151 ± 4 mg per 100 g of froth concentrate compared with 75 ± 3 mg for the heptane extraction. Like the dry extractions, the heptane extract was also purer containing less unidentified matter.

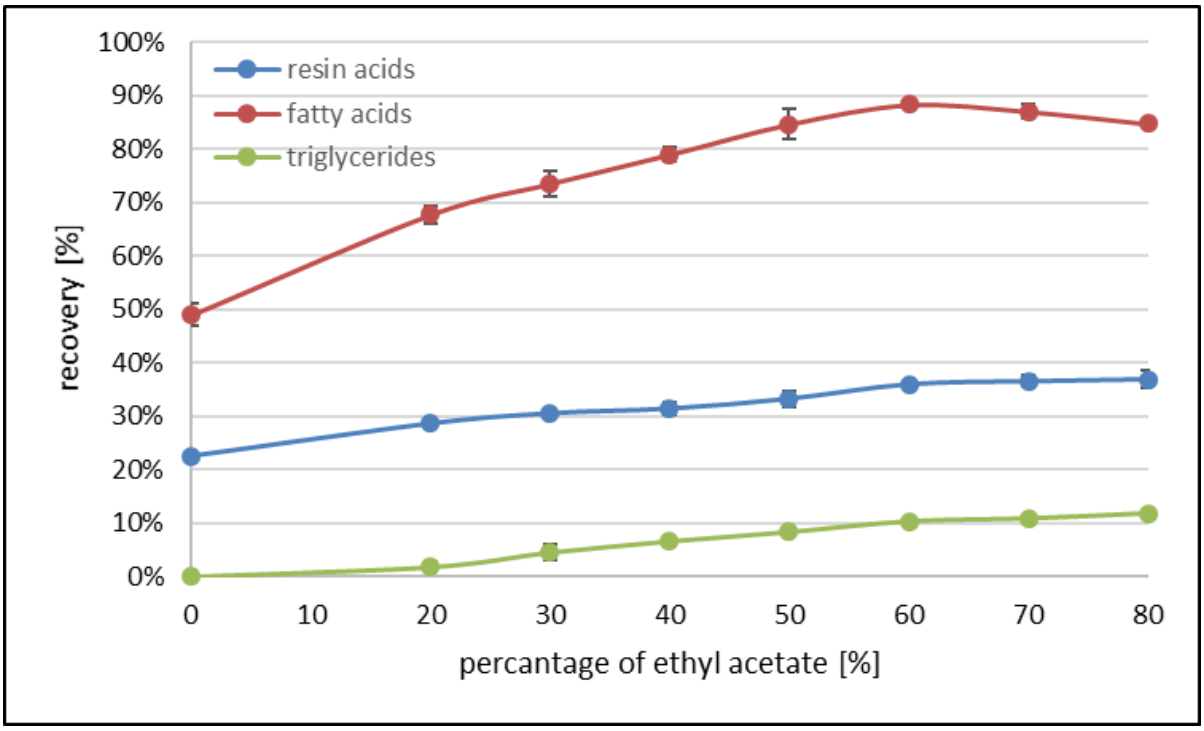


Figure 6-8 Extractives recovery by solvent extraction with heptane/ethyl acetate mixtures

The optimal mixture of ethyl acetate and heptane for recovery of resin acids was 60% ethyl acetate which gave 131 ± 1 mg resin acids per 100 g of froth concentrate. This was therefore chosen as the optimal solvent mixture. This experiment was done by following the same method and using the same batch of froth concentrate as the previous experiment on optimal pH in Figure 6-4. As such, the extract at pH 6 in Figure 6-4 should be identical to the extract at 0% ethyl acetate (100% heptane) in Figure 6-7. However, the extract in Figure 6-7 contains a lower mass of extractives. This is most likely due to a difference in shaking of the samples during extractions. Shaking was done by hand with all samples together in a sample rack for each experiment, such that shaking should be consistent within each experiment but may have varied between experiments. Shaking was gentler for the solvent mixture experiment to reduce the potential for forming an emulsion but appears to have reduced extraction recovery.

6.3 Conclusions

Ultra-filtration, centrifugation and solvent extraction were investigated for recovery of wood extractives from the froth concentrate collected during flotation.

Ultra-filtration removed extractives but with a very slow throughput of less than 60 mL/hr. The DTAB was not separated from the extractives in the filtrate but collected with them on the membrane. Ultra-filtration was therefore deemed not practical.

Centrifugation was able to remove coagulated wood extractives, but this amounted to less than 50% of the total wood extractives removed by flotation so was not considered useful.

Various solvents were investigated for liquid/liquid extraction from the froth concentrate. The less polar heptane and hexane gave the highest recovery of extractives and the purest extract. It is proposed that interactions between extractives and DTAB to form complexes limited the recovery. Electrostatic and hydrophobic interactions appeared to contribute to complex stability. Alteration of pH and solvent polarity resulted in optimal extraction at pH 6 using a 60:40 mixture of ethyl acetate in heptane for resin acids. Triglycerides were poorly extracted presumably due to complexation with DTAB.

Optimal extraction at pH 6 with a 60:40 mixture of ethyl acetate in heptane resulted in 88 ± 1 % recovery of resin acids, 75 ± 1 % fatty acids and 10 ± 0 % triglycerides. DTAB in the aqueous phase was around 150 mg/L which represented only a fraction of the expected 800 mg/L.

Chapter 7 General conclusions

7.1 Factors influencing flotation

Cationic surfactants were found to improve flotation of wood extractives. Of the surfactants investigated, the most effective was DTAB due to its charge, chain length, and hydrophobicity/hydrophilicity balance. Many variables were then investigated for their effect on flotation efficiency. The results are summarised in Table 7-1.

Table 7-1 Summary of factors influencing flotation of wood extractives with DTAB

factor	Effect on flotation efficiency	explanation	Optimal value selected
Process parameters			
DTAB concentration	increase	gives bubbles positive charge	80 mg/L DTAB
Flotation time	increase	Increases total bubble surface area	20 min
Impeller speed	increase	Increases airflow and therefore bubble surface area	1300 rpm (4.5 L/min airflow)
pH	peak at pH 3-5 (colloid flotation) increase (surfactant flotation)	Effect on surface charges changes electrostatic attraction between bubbles and colloids Deprotonation of resin and fatty acids	pH5
Temperature	increase	Unidentified	60°C
Process water composition			
Ionic strength	decrease	Reduces colloid attachment by decreasing Debye length	minimise
Dissolved calcium	decrease	Reduces colloid attachment by decreasing Debye length	minimise
Dissolved wood polymers	decrease	Steric hindrance reduces colloid attachment	minimise
Flocculent (Nalco 6D16)	increase below 0.5 g/L decrease above 0.5 g/L	Small flocs float more easily Large flocs are not floated	minimise

Flotation performed under the identified optimal conditions reduced the extractives concentration by 95% and returned 90% of the water volume for recirculation. The method was also very reproducible, but variation in process water composition meant that substantial variation between batches occurred. The method did however prove effective in treating process water from a second pulp and paper mill despite differences in composition.

With understanding of the factors that influence the flotation of wood extractives, this method could be successfully adopted by industry using flotation equipment already available and in use for flotation deinking.

7.2 Mechanisms of flotation

Several mechanisms for flotation of wood extractives were proposed through the course of this thesis: colloid flotation, surfactant flotation, complex formation, and entrainment of fibre.

Under the optimised conditions (with 80 mg/L DTAB, pH 5, 60 °C, 1300 rpm impeller speed, 4.5 L/min airflow, 20 min flotation time) the dominant flotation mechanism was identified as colloidal flotation. Evidence for this was the high flotation efficiency for triglycerides which were shown to exist predominantly in the colloidal phase (see Table 3-2 and Figure 4-4). Colloidal flotation relies on net attractive surface forces between colloids and air bubbles. The addition of cationic surfactant DTAB provided both an attractive van der Waals component and an attractive electrostatic component. Without surfactant the van der Waals forces would be expected to be repulsive because the effective Hamaker constant for interaction of colloids and air bubbles in water is negative (Equation 9 where $A_{air} < A_{water} < A_{extractives}$ [74, 75]). However, when bubbles are coated by adsorbed surfactant, the interaction can become attractive [116, 117]. Being cationic, the surfactant also rendered the air bubbles positively charged providing electrostatic attraction to the colloids which were negatively charged due to resin and fatty acid anions at their surfaces (see Figure 3-8).

Flotation at low pH without added surfactant was also attributed to colloidal flotation. Though under these conditions the van der Waals interaction would be repulsive, a net attraction could result given an attractive electrostatic interaction between air bubbles which can be positively charged at low pH and the negatively charged colloids.

Colloid flotation appeared to be largely dependent on electrostatic attraction as it occurred when air bubble surfaces were predicted to be positively charged, that is with added cationic surfactants or at low pH values.

The resin and fatty acids were floated separately to the triglyceride component at higher pH values approaching their pK_a values (around 7 for resin acids and around 7-10 for fatty acids [12]). This was explained by surfactant flotation in which the surface-active resin and fatty acid anions adsorb to the air bubble surface and are removed with the froth. Films of fatty acid salts have been found to be most stable at their pK_a due to ion-dipole bonding between carboxylate and carboxyl groups [130] which may contribute to the increased flotation efficiency at pH 7. In the presence of cationic surfactants, resin and fatty acid anions may also be floated by complex formation on the bubble surfaces. The anions would readily interact with surfactant cations adsorbed to bubble surfaces resulting in attachment to the bubbles and removal with the froth.

Entrainment of fibre explained the selective flotation of longer fibres with high extractives content. This mechanism was minimised by using process water with low fibre content.

7.3 Recovery of surfactant and wood extractives

DTAB was found to be removed with the froth during flotation. Separation and recovery of both the DTAB and extractives from the froth concentrate were investigated and proved difficult due to interaction between DTAB and wood extractives. This most likely resulted from complex formation during flotation where DTAB cations on the bubble surface can interact with extractive anions in solution or on colloid surfaces. Ultra-filtration and centrifugation were not found suitable. Optimal solvent extraction was achieved with a 60:40 mixture of ethyl acetate and heptane at pH 6 which resulted in 88% recovery of resin acids, 75% of fatty acids and 10% of triglycerides. Low recovery of triglycerides was attributed to their position at the centre of colloids and to interaction with DTAB. Interaction between wood extractives and DTAB was also observed during ultra-filtration.

7.4 Overall process and recommendations for implementation

The overall processes for flotation removal and solvent extraction recovery are outlined in Figure 7-1. Based on upscaling this process, Table 7-2 presents the potential yield of recovered wood extractives from DAF filtrate process water with a process flowrate of 10 ML/day at the Boyer pulp and paper mill which produces 295 000 tonnes [144] of paper product annually. Although the DAF filtrate was the process stream chosen for research purposes, other process streams may be treated. For example, the method proved to be effective for wood extractives removal from two process streams at a second pulp and paper mill in Albury (Chapter 5.2.5).

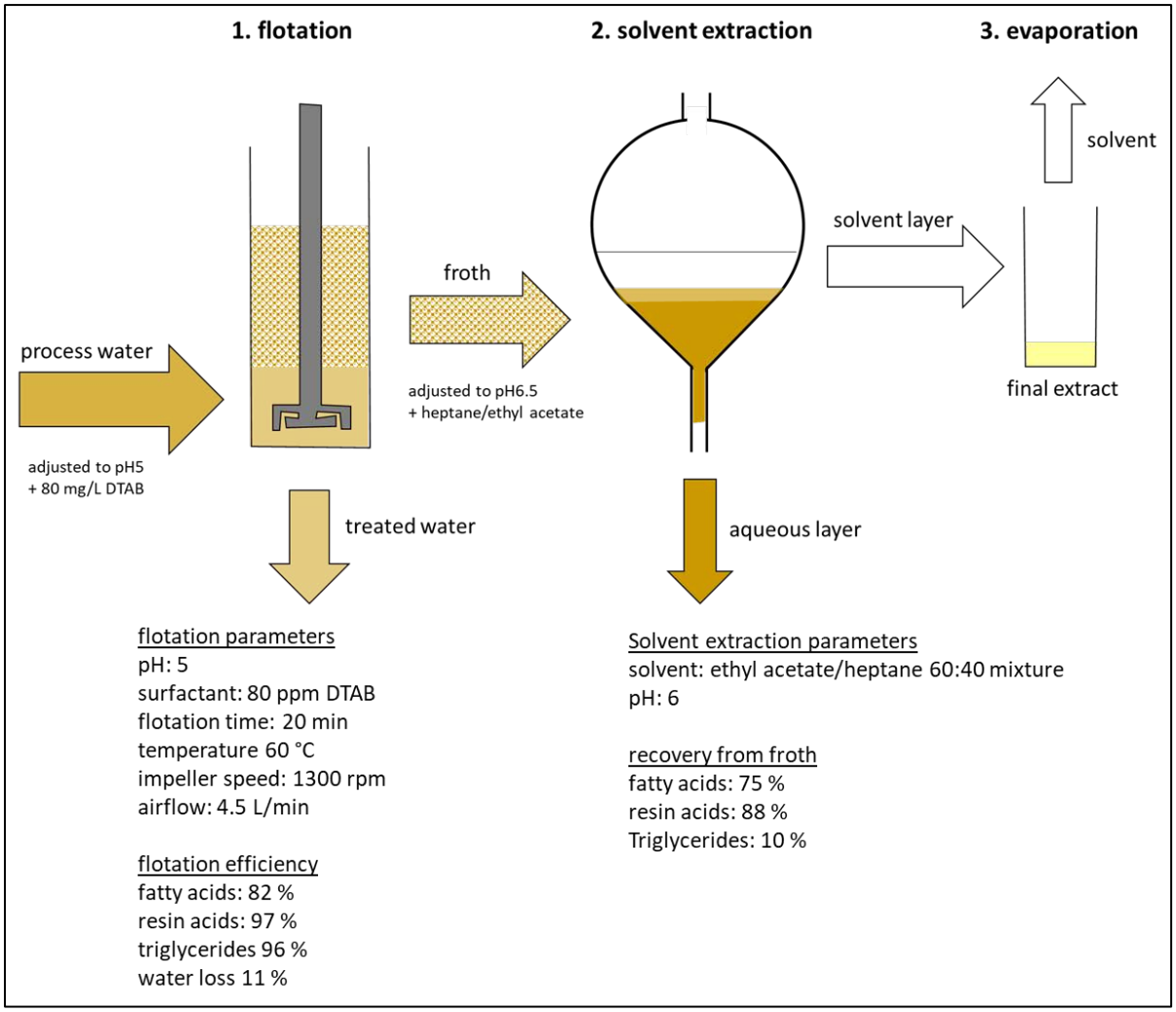


Figure 7-1 Schematic of optimal flotation and recovery processes

Table 7-2 Mill scale yield of wood extractives flotation and recovery

	Fatty acids	Resin acids	triglycerides
extractives removed by flotation [kg/day]	90	1650	860
extractives recovered [kg/day]	68	1450	86
treated water returned:	8.9 ML/day		
mass of DTAB required:	800 kg/day		
based on:			
extractives concentration in process water [mg/L] (mean of 18 DAF filtrate batches listed in Appendix B)	11	170	90
DAF filtrate flowrate at Boyer mill:	10 ML/day		
concentration of DTAB required:	80 mg/L		
optimal flotation efficiency	82%	97%	96%
optimal recovery by solvent extraction	75%	88%	10%

This research has identified the most important factors to consider for efficient flotation: calcium concentration, salt concentration and pH. It also indicated that the presence of other electrolytes inhibit flotation so minimising these is also important. The froth collection method was also shown to be important in reducing water loss. In terms of implementation, this knowledge can be useful in determining an appropriate process stream for flotation treatment, selection of appropriate flotation cell technology and for setting control parameters for the flotation process itself.

The process stream chosen for treatment should be as close as possible to the optimal flotation parameters identified: pH 5, 60 °C temperature, low calcium, low electrolyte concentration, and low dissolved wood polymers. This suggests a stream with minimal addition of chemicals after refining. Fibre content should ideally also be low to prevent fibre loss, as some fibre is removed during flotation. However, fibre was not shown to inhibit flotation of wood extractives, so some fibre loss may be acceptable. The requirements for low calcium, electrolytes and wood polymers should be prioritised because these are not easy to adjust whereas pH and temperature can be adjusted.

Existing flotation technology currently used for deinking could be applied to the flotation process in question. A variety of cell types exist with different methods for bubble generation

and dispersion, collision and froth separation[145]. A froth collection method that allows for drainage of the froth to minimise water loss is recommended. This may be achieved by periodic skimming of the surface or suction of froth above a certain height.

The optimal flotation parameters can then be used to determine control options for the flotation process. pH was found to be very important to optimal flotation so ideally a process stream can be chosen close to the optimal pH. However, the pH could be adjusted prior to the flotation process. This would require measurement of the feed, adjustment by addition of acid or base, and mixing before flotation. The optimal temperature for flotation was shown to be 60 °C, therefore a temperature close to this is desirable. However, temperature had a relatively small effect on flotation efficiency compared to other parameters, so while heating is an option it is energy intensive and may not be cost effective. As 60 °C is close to the typical temperature of TMP process water after the refining process, active heating should not be required.

The treated water quality may be monitored to assess the efficiency of extractives removal. Extractives analysis by GC takes several hours so is not practical for process control. Alternatively, in line turbidity measurements could give a real time measure of extractives content since turbidity correlates very well with colloidal extractives concentrations [94]. The measurements could be used to control water feed into the cell or in a batch process to control the batch cycle time.

Implementation of flotation can be achieved with existing technology that is used for flotation deinking. Recovery by solvent extraction is also possible at industrial scale but there may be alternatives that pose lower safety and environmental risks, such as supercritical carbon dioxide extraction on which there is some research related to wood extractives in the literature [146-148]. The DTAB requirement may be prohibitive unless recovered. Alternatively, flotation without surfactant was shown to be reasonably efficient at low pH. The current study achieved close to 50 % flotation efficiency at pH 2.5, which in a continual process may still effectively reduce the accumulation of extractives in process waters and reduce pitch deposition problems. An additive free process would eliminate the expense and any environmental or safety impact of additives and may also simplify the extractives

recovery process by eliminating problems caused by interaction between extractives and surfactant.

7.5 Recommendations for further work

Recovery of high purity wood extractives and recovery of the surfactant for reuse proved difficult due to interaction between DTAB and the wood extractives. Possible solutions are:

1. Washing with water. It was observed in the current work that dilution of a process water and DTAB mixture before filtration allowed more of the DTAB to pass through the filter (Chapter 6.2.1). Therefore, washing with water should remove the DTAB from wood extractives. This was not pursued in the current work because water efficiency was one motivation for the removal of wood extractives from circulation in the first place. However, it may be possible to recycle the water used for DTAB recovery making this viable.
2. Use of an aliphatic amine in place of the quaternary ammonium salt DTAB. This would allow pH control of its protonation and hence charge and solubility. This may enable flotation to be performed at a low pH at which the amine is protonated and positively charged, and wood extractives are in the colloidal phase and recovery of the surfactant and the extractives at a high pH at which the amine is insoluble but fatty and resin acids dissolve.
3. Alternatives to solvent extraction for recovery of wood extractives from collected froth are possible. For example, there is some evidence in the literature [146-148] that supercritical carbon dioxide extraction is suitable for wood extractives and may be a more feasible and environmental option at industrial scale.
4. Optimisation of flotation without added surfactant. The current study achieved close to 50% flotation efficiency at pH 2.5 by colloidal flotation and around 35% flotation efficiency at pH 7 by surfactant flotation. Although these efficiencies are relatively low and a process at pH 2.5 is likely to be impractical in industry as it would cause corrosion and require subsequent neutralisation, these options may still be worth exploring. In a continual process, even a low efficiency may effectively reduce the accumulation of extractives in process waters. An additive free process would be more easily

implemented and may also simplify the extractives recovery process by eliminating problems caused by interaction between extractives and surfactant.

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Appendix A: Flotation data

Table A-1 Flotation with and without fibre (data for Figure 3-1)

pH	3.0	5.0	6.5	8.0
with fibre, 80 mg/L DTAB	89 ± 1 %	38 ± 2 %	57 ± 2 %	48 ± 7 %
without fibre, 80 mg/L DTAB	76 ± 1 %	28 ± 1 %	45 ± 2 %	48 ± 1 %
with fibre, no surfactant	55 ± 4 %	27 ± 2 %	57 ± 3 %	45 ± 3 %
without fibre, no surfactant	28 ± 7 %	3 ± 10 %	43 ± 2 %	44 ± 2 %

Table A-2 Flotation efficiency with different surfactants (data for Figure 3-6)

pH	**3**	**5**	**7**
DTAB	69 ± 1 %	79 ± 1 %	21 ± 0 %
Quatramine 50	76 ± 1 %	70 ± 1 %	4 ± 6 %
CTAB	61 ± 1 %	40 ± 1 %	16 ± 1 %
Quatramine 16/50	64 ± 0 %	38 ± 0 %	15 ± 1 %
SDS	60 ± 1 %	11 ± 9 %	47 ± 8 %
Triton X-114	7 ± 0 %	26 ± 4 %	41 ± 3 %
Triton X-100	15 ± 3 %	15 ± 3 %	39 ± 1 %
no added surfactant	25 ± 4 %	7 ± 3 %	24 ± 1 %
TMAB	32 ± 1 %	4 ± 4 %	24 ± 2 %

Table A-3 Water loss during flotation with different surfactants (data for Figure 3-7)

pH	**3**	**5**	**7**
DTAB	46 mL	85 mL	114 mL
Quatramine 50	194 mL	154 mL	178 mL
CTAB	157 mL	38 mL	101 mL
Quatramine 16/50	230 mL	77 mL	105 mL
SDS	320 mL	400 mL	530 mL
Triton X-114	160 mL	177 mL	320 mL
Triton X-100	82 mL	230 mL	385 mL
no added surfactant	86 mL	140 mL	94 mL
TMAB	180 mL	156 mL	196 mL

Table A-4 Flotation at different DTAB concentrations (data for Figure 4-1)

DTAB [mg/L]	0	20	40	60	80	100
Resin acids	24 ± 0%	27 ± 0%	67 ± 0%	82 ± 0%	84 ± 0%	85 ± 1%
Fatty acids	24 ± 8%	21 ± 8%	51 ± 1%	69 ± 7%	67 ± 1%	68 ± 1%
Triglycerides	4 ± 2%	12 ± 1%	24 ± 0%	67 ± 0%	96 ± 0%	97 ± 0%
Total extractives	17 ± 1%	21 ± 0%	67 ± 0%	84 ± 0%	88 ± 0%	89 ± 0%
Water loss [mL]	81	35	21	60	117	130

Table A-5 Flotation at different impeller speeds (data for Figure 4-2)

Impeller speed [rpm]	700	1000	1300	1600
Resin acids	11 ± 1 %	63 ± 0 %	80 ± 0 %	88 ± 0 %
Fatty acids	9 ± 3 %	53 ± 1 %	66 ± 3 %	72 ± 1 %
Triglycerides	9 ± 0 %	80 ± 0 %	95 ± 0 %	98 ± 0 %
Total extractives	10 ± 1 %	69 ± 0 %	85 ± 0 %	91 ± 0 %
Water loss [mL]	27	16	83	151

Table A-6 Flotation at different impeller speeds and flotation times (data for Figure 4-3)

Flotation time [min] 1000 rpm	5	10	20	30	40	60
Resin acids	9 ± 1%	31 ± 1%	60 ± 1%	74 ± 0%	88 ± 0%	94 ± 0%
Fatty acids	10 ± 5%	24 ± 5%	42 ± 2%	55 ± 2%	69 ± 2%	76 ± 1%
Triglycerides	9 ± 2%	37 ± 1%	77 ± 0%	93 ± 0%	98 ± 0%	99 ± 0%
Total extractives	9 ± 1%	33 ± 1%	66 ± 0%	81 ± 0%	91 ± 0%	95 ± 0%
Water loss [mL]	-	6	17	50	103	179
Flotation time min 1300 rpm	5	10	20	30	40	60
Resin acids	26 ± 2%	57 ± 0%	74 ± 1%	88 ± 0%	90 ± 0%	-
Fatty acids	19 ± 4%	43 ± 2%	62 ± 1%	76 ± 2%	78 ± 1%	-
Triglycerides	33 ± 1%	75 ± 0%	93 ± 0%	99 ± 0%	99 ± 0%	-
Total extractives	29 ± 2%	63 ± 0%	81 ± 1%	92 ± 0%	93 ± 0%	-
Water loss [mL]	-	24	86	146	195	-
Flotation time min 1600 rpm	5	10	20	30	40	60
Resin acids	31 ± 3%	67 ± 1%	87 ± 0%	95 ± 0%	-	-
Fatty acids	15 ± 5%	52 ± 2%	65 ± 2%	77 ± 2%	-	-
Triglycerides	41 ± 4%	84 ± 0%	97 ± 0%	99 ± 0%	-	-
Total extractives	34 ± 3%	73 ± 0%	90 ± 0%	96 ± 0%	-	-
Water loss [mL]	-	44	144	243	-	-

Table A-7 Flotation efficiency at different pH (data for Figure 4-4)

pH	2.5	3.0	3.5	4.0	4.5
Resin acids	72 ± 0%	79 ± 0%	79 ± 0%	80 ± 0%	79 ± 0%
Fatty acids	64 ± 1%	69 ± 1%	74 ± 3%	75 ± 2%	73 ± 2%
Triglycerides	88 ± 2%	98 ± 0%	99 ± 1%	100 ± 0%	98 ± 0%
Total extractives	77 ± 1%	85 ± 0%	86 ± 0%	86 ± 0%	85 ± 0%
Water loss [mL]	85	115	148	223	161
pH	5.0	5.5	6.0	6.5	7.0
Resin acids	80 ± 0%	78 ± 0%	79 ± 0%	74 ± 1%	77 ± 1%
Fatty acids	69 ± 1%	64 ± 0%	61 ± 1%	44 ± 4%	42 ± 2%
Triglycerides	96 ± 0%	92 ± 0%	78 ± 0%	26 ± 1%	28 ± 2%
Total extractives	85 ± 0%	82 ± 0%	78 ± 0%	57 ± 1%	59 ± 1%
Water loss [mL]	159	121	56	62	61

Table A-8 Flotation with no added surfactant at different pH (data for Figure 4-6)

pH	2.5	3.0	3.5	4.0	4.5
Resin acids	48 ± 1%	34 ± 2%	24 ± 1%	21 ± 0%	23 ± 1%
Fatty acids	49 ± 4%	30 ± 3%	24 ± 7%	18 ± 1%	18 ± 5%
Triglycerides	49 ± 3%	30 ± 2%	12 ± 1%	6 ± 1%	6 ± 3%
Total extractives	49 ± 1%	32 ± 1%	20 ± 1%	16 ± 0%	17 ± 1%
Water loss [mL]	85	115	148	223	161
pH	5.0	5.5	6.0	6.5	7.0
Resin acids	21 ± 0%	28 ± 2%	31 ± 0%	40 ± 1%	47 ± 0%
Fatty acids	13 ± 9%	18 ± 7%	26 ± 3%	25 ± 9%	36 ± 1%
Triglycerides	4 ± 2%	2 ± 3%	7 ± 1%	8 ± 2%	11 ± 3%
Total extractives	15 ± 1%	20 ± 1%	23 ± 1%	29 ± 1%	34 ± 1%
Water loss [mL]	159	121	56	62	61

Table A-9 Flotation efficiency at different temperatures (data for Figure 4-7)

Temperature [°C]	20	30	40	50	60	70
Resin acids	74 ± 2%	84 ± 0%	92 ± 0%	96 ± 0%	97 ± 0%	97 ± 1%
Fatty acids	6 ± 2%	76 ± 0%	81 ± 0%	80 ± 0%	82 ± 0%	80 ± 0%
Triglycerides	74 ± 2%	86 ± 1%	93 ± 0%	93 ± 0%	96 ± 0%	92 ± 0%
Total extractives	73 ± 2%	84 ± 0%	92 ± 0%	94 ± 0%	96 ± 0%	94 ± 0%
Water loss [mL]	125	126	158	105	112	127

Table A-10 Flotation efficiency with each batch (data for Figure 5-1 to Figure 5-6)

DAF Filtrate batch	Total extractives	Fatty acids	Resin acids	triglycerides
22/01/2015	50 ± 1 %	36 ± 2 %	57 ± 1 %	39 ± 5 %
03/03/2015	90 ± 2 %	72 ± 1 %	92 ± 3 %	89 ± 2 %
09/04/2015	85 ± 0 %	69 ± 2 %	80 ± 1 %	96 ± 1%
15/05/2015	85 ± 3 %	65 ± 2 %	80 ± 5 %	95 ± 1 %
30/06/2015	79 ± 1 %	60 ± 2 %	71 ± 1 %	90 ± 1 %
08/09/2015	26 ± 3 %	1 ± 13 %	42 ± 5 %	5 ± 2 %
05/10/2015	40 ± 2 %	16 ± 4 %	59 ± 2 %	8 ± 2 %
26/10/2015	80 ± 1 %	58 ± 9 %	84 ± 1 %	76 ± 2 %
05/01/2016	73 ± 2 %	66 ± 2 %	74 ± 2 %	74 ± 2 %
22/03/2016	42 ± 1 %	8 ± 3 %	50 ± 0 %	27 ± 3 %
13/04/2016	78 ± 1 %	59 ± 5 %	86 ± 2 %	64 ± 1 %
07/06/2016	74 ± 2 %	57 ± 3 %	74 ± 1 %	77 ± 3 %
10/02/2017	66 ± 1 %	38 ± 9 %	84 ± 1 %	34 ± 8 %
22/02/2017	61 ± 0 %	36 ± 7 %	75 ± 1 %	37 ± 1 %
16/05/2017	72 ± 1 %	55 ± 2 %	73 ± 1 %	74 ± 0 %
13/07/2017	41 ± 2 %	49 ± 3 %	51 ± 2 %	24 ± 4 %
21/09/2017	48 ± 1 %	34 ± 3 %	59 ± 1 %	35 ± 1 %
23/01/2018	72 ± 1 %	58 ± 1 %	76 ± 1 %	66 ± 2 %

Table A-11 Flotation with added calcium chloride (data for Figure 5-7)

Added calcium chloride [mM]	0	0.5	1	2	4	8
Resin acids	84 ± 1%	82 ± 2%	79 ± 2%	74 ± 0%	75 ± 2%	65 ± 1%
Fatty acids	68 ± 9%	58 ± 10%	55 ± 4%	48 ± 7%	44 ± 9%	26 ± 4%
Triglycerides	76 ± 2%	76 ± 3%	72 ± 1%	60 ± 2%	62 ± 2%	49 ± 3%
Total extractives	80 ± 1%	79 ± 2%	76 ± 1%	68 ± 1%	69 ± 2%	58 ± 1%
Water loss [mL]	94	75	82	70	83	32

Table A-12 Flotation with added sodium chloride (data for Figure 5-8)

Added sodium chloride [mM]	0	1	2	4	8	17
Resin acids	84 ± 1%	83 ± 1%	81 ± 1%	84 ± 0%	80 ± 1%	73 ± 3%
Fatty acids	68 ± 9%	53 ± 13%	44 ± 11%	51 ± 1%	46 ± 5%	62 %
Triglycerides	76 ± 2%	82 ± 2%	77 ± 1%	80 ± 1%	70 ± 1%	61 ± 3%
Total extractives	80 ± 1%	82 ± 1%	79 ± 1%	82 ± 0%	75 ± 0%	67 ± 1%
Water loss [mL]	94	66	60	48	50	42

Table A-13 Flotation with added dissolved wood polymers (data for Figure 5-9)

Dissolved carbohydrates [g/L]	1.5	2.1	2.6
Resin acids	81 ± 0%	81 ± 1%	75 ± 0%
Fatty acids	63 ± 1%	57 ± 1%	48 ± 1%
Triglycerides	74 ± 2%	67 ± 1%	46 ± 2%
Total extractives	78 ± 1%	76 ± 1%	65 ± 1%
Water loss [mL]	166	95	146

Table A-14 Flotation with added flocculant (data for Figure 5-11)

Flocculant added [mL]	0	0.025	0.1	0.5	1.0
Resin acids	65 ± 0%	85 ± 1%	84 ± 0%	63 ± 1%	33 ± 1%
Fatty acids	58 ± 3%	69 ± 2%	72 ± 5%	50 ± 4%	35 ± 5%
Triglycerides	72 ± 1%	89 ± 0%	91 ± 0%	65 ± 1%	41 ± 2%
Total extractives	68 ± 1%	86 ± 0%	87 ± 0%	63 ± 1%	37 ± 1%
Water loss [mL]	75	93	160	44	57

Table A-15 Concentration of DTAB and extractives during flotation (data for Figure 6-1)

Time [min]	DTAB [mg/L]	Fatty acids [mg/L]	Resin acids [mg/L]	Triglycerides [mg/L]
0	84.98	4.7 ± 0.3	155 ± 1	114 ± 1
5	59.61	4.0 ± 0.0	136 ± 1	90.4 ± 0.2
10	35.4	3.0 ± 0.3	88.1 ± 2.2	47.2 ± 2.2
20	0.06	2.1 ± 0.0	42.0 ± 0.5	12.5 ± 1.0
30	0.00	1.8 ± 0.2	26.0 ± 0.2	4.78 ± 0.10
40	0.02	1.6 ± 0.1	25.1 ± 0.2	4.58 ± 0.04
60	0.01	1.4 ± 0.1	20.9 ± 0.5	3.05 ± 0.05

Table A-16 Flotation efficiency of DTAB and extractives (data for Figure 6-2)

Time [min]	DTAB	Fatty acids	Resin acids	Triglycerides	Total extractives
0	0	0	0	0	0
5	29.9	17 ± 5 %	12 ± 2 %	21 ± 0 %	16 ± 1 %
10	58.3	38 ± 10 %	43 ± 2 %	59 ± 2 %	50 ± 2 %
20	99.9	56 ± 2 %	73 ± 1 %	89 ± 1 %	79 ± 1 %
30	100	62 ± 7 %	83 ± 0 %	96 ± 0 %	88 ± 0 %
40	100	66 ± 3 %	84 ± 0 %	96 ± 0 %	89 ± 0 %
60	100	71 ± 4 %	87 ± 0 %	97 ± 0 %	91 ± 0 %

Appendix B: Characterisation of each process water batch

Table B-1 Characterisation results for each batch of process water

batch		1	2	3	4
source	Screwpress 2	Screwpress 2	Screwpress 2	DAF filtrate	DAF filtrate
date	14/04/2014	14/11/2014	16/12/2014	30/01/2015	03/03/2015
pH	5.18	7.2 ± 0.0	7.4	6.9 ± 0.0	6.8 ± 0.0
Conductivity mS/cm	-	-	1.1	1.1 ± 0.0	0.6 ± 0.0
Calcium mg/L	-	45	45	33	23
Carbohydrates g/L	1.8 ± 0.2	1.6 ± 0.0	1.1 ± 0.0	1.8 ± 0.0	1.3 ± 0.0
Fibre %	0.361 ± 0.003	0.34 ± 0.01	0.35 ± 0.00	0.09 ± 0.00	0.03 ± 0.00
Fibre % in supernatant	-	-	0.04 ± 0.01	0.04 ± 0.01	0.02 ± 0.01
Total extractives mg/L	389 ± 11	490 ± 9	489 ± 6	319 ± 5	249 ± 8
Fatty acids mg/L	16 ± 1	23 ± 1	24 ± 0	17 ± 0	10 ± 1
Resin acids mg/L	251 ± 10	285 ± 4	298 ± 4	190 ± 1	165 ± 2
Triglycerides mg/L	122 ± 2	183 ± 11	168 ± 2	113 ± 3	74 ± 5
dissolved	4 %	14 %	13 %	14 %	10 %
Colloidal	73 %	73 %	77 %	78 %	78 %
Fibre bound	23 %	12 %	10 %	8 %	11 %

batch	5	6	7	8	9
source	DAF filtrate	DAF filtrate	DAF filtrate	DAF filtrate	DAF filtrate
date	09/04/2015	15/05/2015	30/06/2015	08/09/2015	05/10/2015
pH	5.6 ± 0.0	6.5 ± 0.0	6.5 ± 0.0	7.5 ± 0.0	6.6 ± 0.0
Conductivity mS/cm	0.4 ± 0.0	0.5 ± 0.0	0.45 ± 0.00	1.5 ± 0.0	1.3 ± 0.0
Calcium mg/L	15	13	13	47	39
Carbohydrates g/L	1.7 ± 0.0	1.3 ± 0.0	1.6 ± 0.0	2.0 ± 0.0	2.1 ± 0.0
Fibre %	0.04 ± 0.00	0.05 ± 0.00	0.07 ± 0.00	0.09 ± 0.00	0.03 ± 0.00
Fibre	0.04 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.03 ± 0.00	0.02 ± 0.00
Total extractives mg/L	214 ± 2	247 ± 2	294 ± 13	280 ± 5	220 ± 2
Fatty acids mg/L	9 ± 0	8 ± 0	7 ± 3	4 ± 0	5 ± 0
Resin acids mg/L	135 ± 1	149 ± 2	173 ± 6	160 ± 3	132 ± 1
Triglycerides mg/L	70 ± 2	89 ± 1	114 ± 4	116 ± 2	83 ± 1
dissolved	6 %	12 %	14 %	25 %	18 %
Colloidal	75 %	78 %	80 %	74 %	81 %
Fibre bound	18 %	10 %	6 %	2 %	0 %

batch	10	11	12	13	14
source	DAF filtrate	DAF filtrate	DAF filtrate	DAF filtrate	Albury TMP effluent
date	26/10/2015	05/01/2016	22/03/2016	13/04/2016	02/06/2016
pH	6.3 ± 0.0	6.0 ± 0.0	7.2 ± 0.0	6.3 ± 0.0	4.7 ± 0.0
Conductivity mS/cm	0.67 ± 0.00	0.50 ± 0.01	1.30 ± 0.02	0.64 ± 0.01	0.33 ± 0.01
Calcium mg/L	20	13	65	31	20
Carbohydrates g/L	1.9 ± 0.0	1.70 ± 0.03	2.12 ± 0.04	1.71 ± 0.08	1.39 ± 0.03
Fibre %	0.034 ± 0.001	0.069 ± 0.003	0.058 ± 0.002	0.023 ± 0.003	0.314 ± 0.018
Fibre	0.007 ± 0.001	0.009 ± 0.001	0.014 ± 0.005	0.007 ± 0.001	0.033 ± 0.002
Total extractives mg/L	221 ± 1	298 ± 1	280 ± 2	172 ± 2	921 ± 32
Fatty acids mg/L	5 ± 0	18 ± 0	13 ± 0	9 ± 0	32 ± 1
Resin acids mg/L	130 ± 1	202 ± 1	195 ± 1	116 ± 2	700 ± 26
Triglycerides mg/L	85 ± 0	78 ± 1	72 ± 2	48 ± 1	189 ± 6
dissolved	12 %	12 %	25 %	15 %	1 %
Colloidal	81 %	74 %	69 %	82 %	36 %
Fibre bound	7 %	13 %	6 %	3 %	63 %

batch	15	16	17	18	19
source	Albury DAF feed	DAF filtrate	DAF filtrate	DAF filtrate	DAF filtrate
date	02/06/2016	07/06/2016	10/02/2017	22/02/2017	16/05/2017
pH	5.7 ± 0.0	5.6 ± 0.0	6.7 ± 0.0	7.2 ± 0.0	6.7 ± 0.0
Conductivity mS/cm	1.43 ± 0.07	0.55 ± 0.01	1.25 ± 0.01	0.79 ± 0.00	0.49 ± 0.00
Calcium mg/L	104	17	40	31	26
Carbohydrates g/L	3.06 ± 0.02	2.02 ± 0.03	1.84 ± 0.05	1.81 ± 0.03	1.66 ± 0.02
Fibre %	0.086 ± 0.003	0.045 ± 0.006	0.021 ± 0.003	0.031 ± 0.001	0.176 ± 0.001
Fibre	-0.001 ± 0.001	0.018 ± 0.003	0.007 ± 0.003	0.004 ± 0.000	0.013 ± 0.005
Total extractives mg/L	140 ± 6	284 ± 14	167 ± 8	267 ± 22	462 ± 4
Fatty acids mg/L	19 ± 1	7 ± 0	12 ± 2	16 ± 6	17 ± 0
Resin acids mg/L	85 ± 3	183 ± 13	111 ± 5	169 ± 15	249 ± 7
Triglycerides mg/L	35 ± 4	94 ± 3	44 ± 3	83 ± 2	196 ± 2
dissolved	14 %	8 %	23 %	18 %	28 %
Colloidal	32 %	88 %	71 %	72 %	64 %
Fibre bound	54 %	4 %	6 %	10 %	8 %

batch	20	21	22	23	24
source	Screwpress 2	DAF filtrate	Screwpress 2	DAF filtrate	DAF filtrate
date	16/05/2017	13/07/2017	13/07/2017	21/09/2017	23/01/2018
pH	6.8 ± 0.0	7.3 ± 0.0	7.3 ± 0.0	6.1 ± 0.0	6.7 ± 0.0
Conductivity mS/cm	0.54 ± 0.01	0.84 ± 0.00	0.88 ± 0.01	0.95 ± 0.00	0.51 ± 0.00
Calcium mg/L	30	37	42	32	18
Carbohydrates g/L	1.77 ± 0.04	1.92 ± 0.06	1.82 ± 0.00	1.84 ± 0.05	1.58 ± 0.04
Fibre %	0.381 ± 0.001	0.074 ± 0.002	0.339 ± 0.002	0.036 ± 0.001	0.072 ± 0.004
Fibre	0.036 ± 0.026	0.032 ± 0.002	0.041 ± 0.003	0.012 ± 0.002	0.031 ± 0.002
Total extractives mg/L	584 ± 11	364 ± 8	549 ± 10	283 ± 0	285 ± 6
Fatty acids mg/L	17 ± 5	14 ± 1	19 ± 3	11 ± 1	12 ± 0
Resin acids mg/L	327 ± 2	216 ± 2	336 ± 7	158 ± 1	189 ± 4
Triglycerides mg/L	240 ± 7	135 ± 5	194 ± 0	113 ± 0	84 ± 3
dissolved	41 %	16 %	13 %	9 %	17 %
Colloidal	47 %	77 %	77 %	81 %	69 %
Fibre bound	13 %	8 %	10 %	10 %	14 %

Appendix C: Zeta potential data (for Figure 3-8)

	Wood extractive colloids			Wood extractive colloids with 80 mg/L DTAB		
pH	**Conductivity mS/cm**	**Zeta potential mV**	**Standard deviation**	**Conductivity mS/cm**	**Zeta potential mV**	**Standard deviation**
2.97	2.35	-2.72	4.83	2.35	-3.40	3.92
3.49	1.96	-4.45	4.35	1.95	-4.62	3.92
4.00	1.77	-6.20	4.92	1.79	-7.39	5.47
4.50	1.68	-7.36	4.46	1.66	-7.61	4.91
4.99	1.52	-7.60	4.57	1.57	-8.07	4.78
5.42	1.41	-8.07	4.23	1.45	-7.80	4.97
6.00	1.41	-8.42	4.53	1.41	-7.96	4.33
6.49	1.37	-8.91	4.99	1.39	-7.73	3.90
6.98	1.34	-9.02	4.48	1.36	-8.11	4.37
7.53	1.31	-9.21	5.23	1.30	-8.56	4.40
7.99	1.33	-8.87	4.08	1.37	-9.49	3.90

Appendix D: Residual plots for linear regression

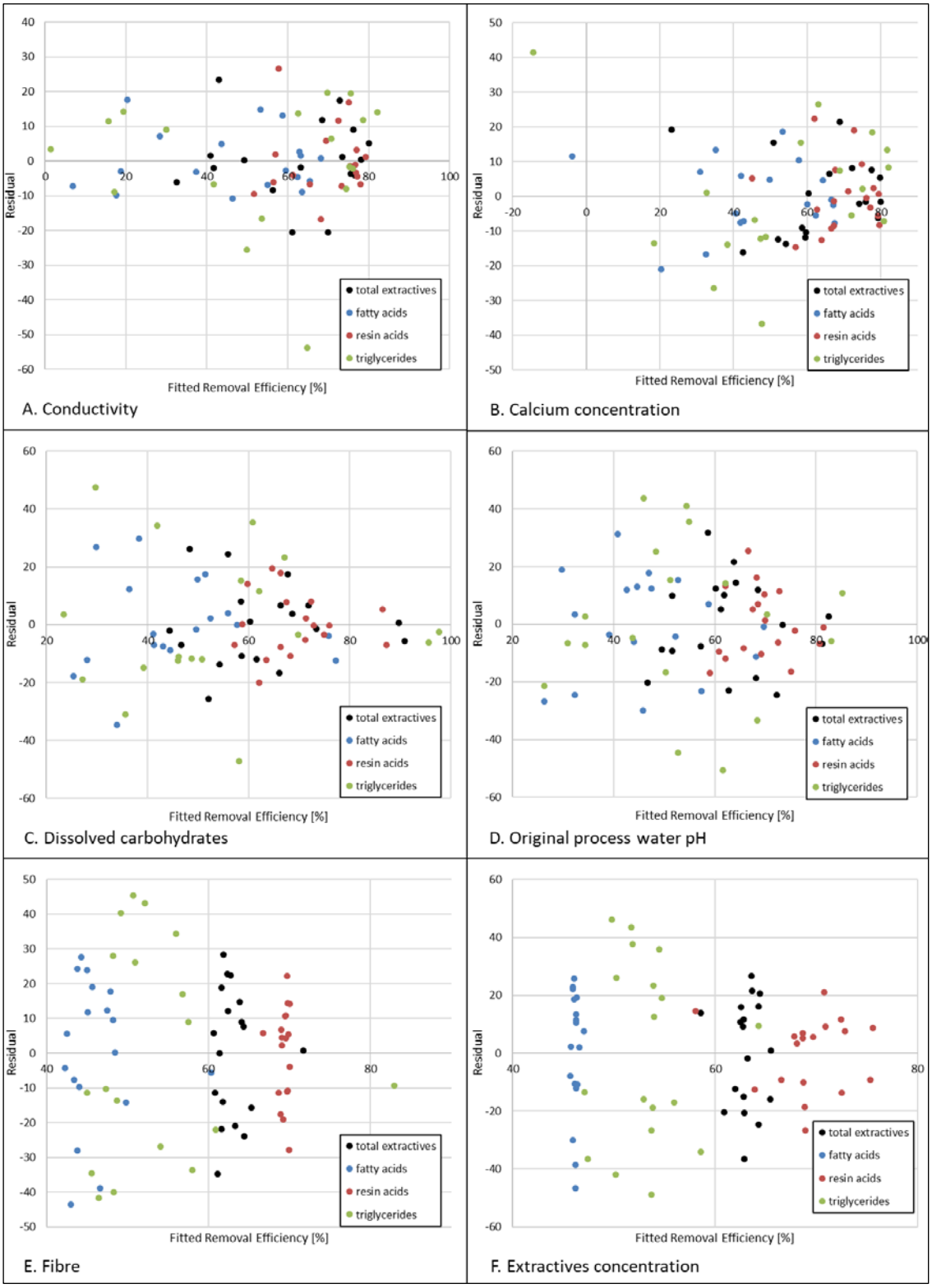

Figure C-1 Residual plots for regression analysis

Appendix E: List of Publications

Conference papers:

Singh, S., K. Stack, T. Lewis and D. E. Richardson (2014). *Comparison of foaming agents for selective froth flotation of wood extractives from Pinus radiata TMP process water.* Fibre Value Chain Conference and Expo 2014, Rotorua, New Zealand, Appita Inc.
(based on work presented in Chapter 3)

Singh, S., K. Stack, T. Lewis and D. E. Richardson (2018). *Wood extractives recovery from flotation of thermo-mechanical pulp process water.* Pan Pacific Fibre Value Chain Conference 2018, Rotorua, New Zealand, Appita Inc.
(based on work presented in Chapter 6)

Peer reviewed conference paper:

Singh, S., K. R. Stack, T. W. Lewis and D. E. Richardson (2015). *Examination of variables influencing the selective froth flotation of wood extractives from Pinus radiata TMP process water.* Fibre Value Chain Conference and Expo 2015: Pulp and Paper Bioenergy Bioproducts, Melbourne, Australia, Appita Inc.
(based on work presented in Chapter 4)

Peer reviewed Journal papers:

Singh, S., K. R. Stack, T. W. Lewis and D. E. Richardson (2016). *Optimisation of froth flotation for removal of wood extractives in paper manufacture.* Appita Journal 69(3): 253-263.
(based on work presented in Chapters 4 and 5)

Singh, S., K. Stack, T. Lewis and D. E. Richardson (2019). *Wood extractives recovery from flotation of thermo-mechanical pulp process water.* Appita Journal 72(3): 135-149
(based on work presented in Chapter 6)